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Agriculture Development Fund

FINAL REPORT

PRODUCTION OF DIESEL FUEL LUBRICITY ADDITIVES FROM VARIOUS VEGETABLE OILS

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Production of Diesel Fuel Lubricity Additives From Various Vegetable Oils

Project No.: 98000081

Final report for the period of December 1, 1998 – December 1, 2000

For

The Saskatchewan Agriculture Development Fund

By

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A. ABSTRACT

This report summarizes the development of a vegetable oil based fuel additive technology. A total of 12 biodiesel esters were prepared by reacting canola, linseed, rapeseed and sunflower oils with methanol, ethanol, 2-propanol and butanol in the presence of alkali catalysts. The esters were extensively analyzed for their chemical and physical properties, including lipid and fatty acid compositions, densities, viscosities, cloud and pour points, acid values, iodine values, heats of combustion and volatility behaviors. The esters were further lubricity tested in a precision M-ROCLE bench machine. When blended at 1 vol% treat rate with a reference fuel, all 12 esters enhanced the fuel's Lubricity Number. In particular, two esters made from canola oil increased the Lubricity Number of the reference fuel by 59% and 67%. Canola methyl ester, even at a 0.1% treat rate, continued to show sufficient lubricity improvement. A continuous flow process for the canola methyl ester production was accordingly developed. The production cost was estimated at $0.72 per liter of CME for 1 million liters per year plant capacity. The potential capital returns were also calculated.

B. EXECUTIVE SUMMARY

Mono lower alkyl esters produced from vegetable oils, such as canola and soybean oils, are known as biodiesel. Biodiesel has been widely used in Europe as an environmentally friendly, renewable diesel fuel substitute. In Canada, different tax structures have so far disfavored biodiesel fuels from competing with conventional diesels; however, many non-fuel applications of biodiesel have been explored. Among them, use of biodiesel as a diesel fuel lubricity additive is particularly promising.

The goal of this research project is to develop a vegetable oil based fuel lubricity additive technology in Saskatchewan. The project's scope included the preparation of esters from low-grade vegetable oils by reacting oils with alcohols in the presence of catalysts. The esters thus produced were characterized for their properties related to lubricity fuel additives. It is desired to create a continuous flow process to make the esters as cheaply and efficiently as possible, and thus to design feasible, scaleable processes for ester production when industrial and economic conditions warrant.

Over the past two years, significant progress has been made according to the project plan. Several batch preparation methods have been developed and used to systematically prepare 12 different biodiesel esters from four vegetable oils: canola, linseed, rapeseed, and sunflower oils, and four alcohols: methanol, ethanol, 2-propanol, and butanol. The chemical compositions and various physical and fuel properties of the esters have been determined. In particular, a modified lubricity bench test machine has been employed to evaluate and compare the tribological performance of these esters as

diesel fuel lubricity additives. When blended at 1% by volume in a reference diesel fuel, each of the 12 esters has been found capable of adequately increasing the fuel lubricity. In particular, two canola based esters, namely canola 2-propyl ester and canola methyl ester, are found to be the top two effective additives, bringing in improvements of 67% and 59%, respectively, in Lubricity Number over the reference fuel. These two esters are also effective when used at treat rate below 1%.

Because the production of canola methyl ester (CME) is more technically simple and economically feasible than that of 2-propyl ester, we have selected canola methyl ester as the best candidate for a lubricity additive development. Accordingly, a continuous flow process has been designed for making canola methyl ester. Cost analyses and parameter sensitivity analyses are then performed for a 1 million liters CME per year plant. It is estimated that the total capital costs requires $350,000, while the canola methyl ester can be produced at a cost of $0.72 per liter. The price of the oilseed will have the greatest impact on the production cost. Furthermore, assuming one-dollar per liter profit of canola methyl ester sold as a bulk fuel lubricity additive, an annual after tax net profit would be over $700,000. The numbers indicate a profitable opportunity for the CME project.

Saskatchewan is a major producer of canola oilseeds. At present, most food grade canola produced in the province is exported as unprocessed raw material. Because of a number of problems, including the transportation bottleneck, the profit of growing canola is declining, and the canola acreage in Western Canada is dropping in recent years. Therefore, a successful development of a value-added, canola based fuel additive product shall expand market for canola, and increase financial benefits to producers and

processors. In addition, a large amount of low-grade oilseeds, unfit for human consumption, is left without utilization each year. The inclusion of low-grade oils, such as those from heat damaged seeds and/or from green seeds for the ester production would bring in new income to farmers.

C. TECHNICAL REPORT

1. Background

1.1. Biodiesel, An Overview

Biodiesel is defined as the mono, lower alkyl esters of fatty acids obtained from renewable lipid resources such as animal fats and vegetable oils. Vegetable oils are mainly triglycerides, which are esters of the trihydric alcohol, glycerol, combined with three molecules of long-chain fatty acids. These fatty acids often differ by the length of the carbon chains (varying from 12 – 22 carbons), as well as the number, position and orientation of double bonds in the carbon chains. The viscosity of vegetable oils is of the order of 10 to 20 times that of diesel fuel. When used neat as fuels, they cause injector fouling and other engine problems. The methyl or ethyl esters of vegetable oils have viscosities approximately twice that of diesel fuels. Therefore, the biodiesel esters can be used directly or as blends with diesel fuel in a diesel engine (1). Biodiesel is a biodegradable and renewable fuel. It contributes little net greenhouse gases or sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on biodiesel.

Biodiesel is commonly synthesized by a reaction called transesterification, in which vegetable oil is mixed with a lower monoalkyl alcohol in the presence of an alkali catalyst to yield esters and glycerol (glycerin) (2). The most commonly used alcohol is methanol because of its lower price than other monoalkyl alcohols. Much work has been

done in the past two decades on the production and real-world market performance of biodiesel, which has been reviewed recently by Knothe et al. (3). Rapeseed, canola, sunflower, soybean oils, beef tallow and many other oils have been used for the production of biodiesel esters (4-11). For instance, Peterson et al. (10) reported detailed batch transesterification procedures for methyl and ethyl esters of four lipids using KOH catalyst at room temperature. They found that use of absolute ethanol was essential to successful production of ethyl esters, which was characterized by the formation of two liquid phases: ester and denser glycerol phases at the end of the reaction. Ahn et al. (12) carried out methyl ester transesterification of rapeseed oil in two steps and achieved a 99% yield. During the soybean methyl ester preparation, Boocock (13, 14) added tetrahydrofuran as a co-solvent to transform the oil/methanol two-phase system into a one-phase system. As a result, the mass transfers between the reactants were enhanced, and the methanolysis process was completed in a few minutes. Compared with the common methyl esters, branched-chain esters greatly reduced the crystallization onset temperature of neat esters and ester diesel fuel blends. For example, 2-propyl and 2-butyl esters of soybean oil crystallized 7 to 11 and 2 to 14°C lower, respectively, than the soy methyl esters (15).

Often, the vegetable oils of choice for biodiesel production are those which occur abundantly in the region of testing. Therefore, rapeseed oil is the primary biodiesel source in Europe while both rapeseed and soybean oils are used in the United States. Canola oil is a cultivated version of rapeseed oil, which contains very little erucic acid and is now widely produced in Western Canada. Therefore, canola oil along with

rapeseed, linseed (flax) and sunflower oils, all available in the prairie provinces, are the ideal feed stock selections for biodiesel production in Saskatchewan.

Biodiesel, primarily rapeseed methyl ester, has been in commercial use as an alternative fuel since 1988 in many European countries, including France, Austria, Germany, Sweden, Italy, Belgium, Hungary and Czech Republic (15-18). A 90% tax deduction proposed by the European Community for the use of biodiesel enables it to be sold in Europe at prices competitive to conventional diesel fuel. The total European production of biodiesel for 1997 was estimated at 660 thousand tons. In the United States, biodiesel, primarily made from soybean oils, also is being commercialized. Several demonstration programs used biodiesel to fuel municipal buses, trucks and construction equipment (19). In Canada, the Canadian Renewable Fuels Association (CRFA), whose members include the Saskatchewan Canola Development Commission and the Ontario Soybean Growers' Marketing Board, promotes renewable bio-fuels (ethanol, biodiesel) for automotive transportation through consumer awareness and government liaison activities. However, the suggested 20% biodiesel blended diesel fuel currently costs approximately ten cents more per blended liter than the conventional diesel due to high feed cost of vegetable oil, thereby preventing its large-scale use in North America.

1.2. Biodiesel as Fuel Lubricity Additive

Various non-fuel uses of biodiesels have been investigated. For example, soybean methyl ester has been tested for cleanup of petroleum oil spills. Also, the soy ester is reported having market potential as paint strippers and solvents for industrial

cleaning (20). Another promising application of biodiesel is as a diesel fuel lubricity additive (21, 22).

Fuel lubricity is defined as how well a fuel provides lubrication to the fuel system and engine, thereby reducing component wear and friction. Polar hetero-cyclic compounds containing N and/or O atoms have recently been viewed as potent lubricity agents naturally present in diesel fuels (23). Environmental concerns have prompted regulations to limit the sulfur in diesel fuels. During hydrotreating for sulfur removal from diesel fuels, the N and O containing compounds have also been inevitably removed. Though the low sulfur, low nitrogen diesel fuel decreases pollution, it also results in shorter diesel injection pump and engine lives because of insufficient lubrication (24). Canada has mandated a sulfur content below 0.05 wt% (500 ppm) in diesel fuel since 1994, and has experienced more problems with its low sulfur winter diesel fuel. This is due to fuel's low viscosity and pour point so as to improve the cold flow characteristics of the fuel. As a result, Canadian fuels recently have been ranked low among those possessing for their worst lubricity in the world (25). To alleviate this problem, the refiners routinely blend lubricity additives into their fuels.

Lubricity additives are substances that are added to carrier fuels (oils) for the purposes of lowering friction and/or reducing wear during sliding. The lubricity additives currently used in diesel fuels range from fatty acids, alkyl amines, esters of natural acids to fully synthetic non acidic products. Several of the recent studies performed at the University of Saskatchewan have also shown that when biodiesel esters were added to a low lubricity, hydrotreated Canadian winter diesel fuel at treatment rates in the order of 0.5-2 vol%, they significantly improved the lubricity of the fuel (21, 26).

It may be noted that the consumption of transportation diesel fuel in Canada has steadily increased by some 50% from 1991 to 1998, and this trend is predicted to continue in the coming years. In 1999, the Canadian annual diesel fuel consumption had reached about 40 billion liters. Of this quantity, approximately 60% is for on-road uses (trucking), while the remaining 40% is for off-road uses (marine, rail, machinery, etc) (27). If biodiesel esters are adopted as a fuel lubricity additive even at 0.1% treat rate, the market demand for biodiesel as lubricity additives alone could be 40 million liters per year in Canada.

1.3. Fuel Lubricity Evaluation

There are many different types of diesel fuel lubricity-testing equipment in existence. Some of the most common tribological procedures are outlines below (24).

The European-developed High Frequency Reciprocating Rig (HFRR) is one of the most widely used diesel fuel lubricity-testing apparatuses. This machine consists of a vertically loaded ball reciprocating against a flat polished steel plate at 50Hz. The maximum wear scar diameters acceptable are 380 μm at 25°C and 450 μm (ISO) or 460 μm (CEN) at 60°C.

The Scuffing Load Ball on Cylinder Lubricity Evaluator (SLBOCLE), developed in the USA, is another widely used lubricity bench test. The fuel lubricity test employs a loaded ball on a rotating cylinder configuration. The applied load that causes adhesive wear between the two contacting test specimens is used to compare test fuels. The load is increased stepwise until the onset of scuffing. Fuels that result in SLBOCLE loads below 3000 g are considered inadequate, requiring lubricity additive.

Another USA developed lubricity bench test, the Lubrizol/Hadley BOCLE, is also used for diesel fuel lubricity testing. This apparatus employs the same configuration as the SLBOCLE except that the L/H BOCLE incorporates a constant load and then uses the circular wear scar diameter to distinguish the test fuel's lubricity. If the wear scar diameter under the test conditions is greater than 460 μm, the test fuel is unacceptable.

Both the HFRR and SLBOCLE have difficulties evaluating the effectiveness of diesel fuel lubricity additives. Each test is believed to underestimate the additive's effectiveness at low or high concentrations. Correlation between the HFRR and SLBOCLE tests is relatively poor.

Full-scale injection pump apparatuses are also used for diesel fuel lubricity testing. These tests are more time consuming and costly than the bench tests. In addition, these are often one of a kind machines owned by the individual company and little work is openly published.

In the Department of Mechanical Engineering at the University of Saskatchewan, Galbraith and Hertz (26) developed a Roller on Cylinder Lubricity Evaluator (ROCLE). Both wear scar area and friction of coefficient were used to calculate a dimensionless Lubricity Number (LN) of the fuel. The first generation of the ROCLE had an average LN coefficient of variation up to 10% based on 12 tests when discarding two outliers. Many improvements and computer interfacing of the original ROCLE were implemented during this project to achieve a more precise "M-ROCLE" tribology testing machine (details see Section 4.3.1).

1.4. Biodiesel Process Patents

Renewed interests in biodiesel as an alternative fuel or as a fuel additive have brought about many patents on biodiesel production and processing. Table 1 lists 21 recent Canadian and US patents, arranged by the patent issue date. Each entry includes patent number and its issue date, the title, as well as the patent assignee or inventor(s) and their country origin. All these patents emphasize the engineering improvement of the biodiesel process. Instead of commenting on the merits of individual patents, the useful inventions are assorted and summarized in the following paragraphs into different unit operations associated with the biodiesel production, starting from pretreatment of raw oils, to transesterification and separation, and finally to purification of by-product glycerol.

Table 1. List of recent North America patents on biodiesel production.

Patent number, Issue date	Patent title	Assignee/inventor* (country origin)
US 6,090,959, July 18, 2000	Method of producing fatty acid lower alkylester from fat and oil	Lonford Dev. Ltd. (JP)
US 6,015,440, Jan. 18, 2000	Process for producing biodiesel fuel with reduced viscosity and a cloud point below -32°F	Univ. Nebraska, (NE, US)
US 5,972,057, Oct. 26, 1999	Method and apparatus for producing diesel fuel oil from waste edible oil	Lonford Dev. Ltd. (JP)
US 5,908,946, June 1, 1999	Process for the production of esters from vegetable oils or animal oils and alcohols	Institut Francais du Petrole (FR)
US 5,885,946, March 23, 1999	Process for preparing a synthetic ester from a vegetable oil	Raision Tehtaat Oy Ab (FL, US)
US 5,849,939, Dec. 15, 1998	Method for the preparation of fatty acid alkyl esters	Vogel & Noot (AT)
US 5,773,636, June 30, 1998	Process for the production of fatty acid lower alkyl esters	US 5,773,636, June 30, 1998

Table 1. List of recent North America patents on biodiesel production (cont.).

Patent number, Issue date	Patent title	Assignee/inventor* (country origin)
US 5,730,029 March 24, 1998	Esters derived from vegetable oils used as additives for fuels	Lubrizol (OH, US)
US 5,713,965, Feb. 3, 1998	Production of biodiesel, lubricants and fuel and lubricant additives	Foglia* (FL, US)
Us 5,710,030, Jan. 20, 1998	Process for preparing fuels, fuel substitutes, and fuel supplements from renewable resources	Henkel (PA, US)
US 5,525, 126, June 11, 1996	Process for production of esters for use as a diesel fuel substitute using a non-alkaline catalyst	Agri. Utilization Res. Int. (MN, US)
US, 5,514,820, May 7, 1996	Continuous process for the production of lower alkyl esters	Henkel (DE)
CA 2,131,654, March 09, 1996	Process for producing lower alkyl fatty acid esters	Boocock* (CA)
US 5,455,370, Oct. 3, 1995	Process for the production of fatty acid lower alkyl esters	Henkel (DE)
US 5,434,279, July 18, 1995	Process for preparing fatty acid esters of short-chain monohydric alcohols	Vogel & Noot (AT)
US 5,424,467, June 13, 1995	Method for purifying alcohol esters	Idaho Res. Found. (ID, US)
US 5,424,466, June 13, 1995	Improved process for the production of esters from fatty substances having a natural origin	Institut Francais du Petrole (FR)
US 5,399,731, March 21, 1995	Process for the production of fatty acid esters of lower alcohols	Vogel & Noot (AT)
US 5,354,878, Oct. 11, 1994	Process for the continuous production of lower alkyl esters of higher fatty acids	Connemann* (DE)
US 5,116,546, May 26, 1992	Process for producing fatty-acid lower alkyl mono-esters	Van den Bergh Foods (IL, US)
US 4,652,406, March 24, 1987	Process for the production of fatty acid alkyl esters	Henkel (DE)

Pretreatment of raw oil and catalyst

The raw natural oils can be treated with bleaching earth to remove shell remains and mucins (US Patent 5,773,636), to obtain a substantially odorless and light-colored product. If raw oils contain high concentration of free fatty acids, the free acids are converted to esters in a preliminary esterifying step by reacting with methanol and an acidic catalyst (US 4,562,406). The resulting reaction mixture is then separated into an alcohol phase and an oil phase; the latter is extracted with an immiscible extractant to remove residual water before being fed to the main transesterification stage.

US 5,972,057 claimed that dissolving the catalyst in methanol prior to the reaction could accelerate the reaction between the alcohol and waste edible oil, as compared with the method of adding catalysts directly into a reactor. For example, 99% oil conversion was reached in 1.0 min at 60°C when using pre-dissolved catalyst, while 96% conversion was reached in 30 min under the same conditions when methanol and catalyst were added to the oil simultaneously.

Two-step transesterification

Many patents have applied two or multiple transesterification steps to achieve high conversion (99%). For instance, the Vogel & Noot process in US 5,399,731 uses unpurified natural oils and fats with up to 20% of free fatty acids in a 2-step process to obtain high degree of transesterification. The reaction is carried out at ambient temperature and atmospheric pressure in the presence of a basic catalyst with an excess of methanol. In a later Vogel patent (US 5,434,279), the glycerin phase produced after the first step is at least partially added to the reaction mixture after the second esterification, to facilitate the subsequent phase separation. The Vogel process is carried out without

pressure and heat supply, thus uses simple equipment, and produces a high degree of purity of fatty acid esters.

US 5,514,820 (Henkel) relates to a continuous process using oils containing less than 1% free fatty acid and operating at temperature and pressure less than 100°C and 10 bar, respectively. The reaction takes place through a tubular reactor followed by a horizontal static separator in each of the two stages. To ensure thorough mixing by turbulence in the reactor, the Reynolds number of the reaction mixture is maintained greater than 2,300 (calculated for the entrance of the first tube reactor).

Process in US 5,354,878 implements a more complex reactor arrangement in its two-step transesterification. Each step includes a first column reactor in which the feed flow rate is lower than the sinking rate of the glycerin separated from the reaction mixture, followed by a continuous stirred tank reactor (CSTR) for further transesterification.

Separation of glycerol phase after the transesterification

The separation of the crude ester and glycerin phases is often done in a gravity separator (e.g., US 5,434,279). US 5,354,878 uses a plate separator, which is simple but more efficient. Centrifuge can also be used but is much more energy inefficient.

Purification of crude ester

The crude ester phase consists of fatty acid lower alkyl monoesters, unreacted triglycerides, soap, and residual catalyst. The removal of excess alcohol has been done by means of a falling-film evaporator, or bubbling air, nitrogen or water vapor through it (US 5,434,279), or by stripping (US 5,354,878). Then, the spent catalyst is removed by

washing with small amount of water or diluted acid followed by liquid-solid separation (US 5,399,731, US 5,434,279).

Crude ester is also treated with solid extraction (US 5,972,057) to remove residual catalyst, odor material, coloring material and moisture. In this patent, the preferred absorbent was acid clay treated with sulfuric acid at size of 0.1- 1.5 mm. After solid extraction, the solid absorbents containing the impurities were separated by centrifuge. The Patent claims that this purification process is simple as compared with the processes of removing residual catalyst by warm water or neutralizing acid, since there is no more possibility of accelerating the saponification, nor need of removing water after washing.

US 5,424,467 proposes one-step liquid (solvent) extraction for removing unreacted alcohol and catalyst from the raw ester. Conventional extraction design is recommended to provide adequate contact between the crude ester phase and the solvent, including mixer settlers, vertical towers of various kinds that operate by gravity flow, agitated tower extractors, and centrifugal extractors. The solvent to crude ester ratio is preferably varied between 1:1 to 1:4. In US 5,424,467, purified glycerol is used as the extraction solvent. The purity of extract stream of ester is higher than 99%, containing less than 100 ppm of residual catalyst. Ester of this purity generally does not need to be washed to remove impurities when used as an alternative fuel.

A three-step purification scheme is proposed in US 5,116,546. First, the excess methanol is distilled off and recirculated to the reactor. Then, the catalyst and soap components are removed by conventional water washing and filtration steps, and are used as a feedstock for soap production. Finally, the ester phase is submitted to another distillation step in which the high purity monoesters are separated from a distillation

residue, which consists of a mixture of unreacted triglycerides and remaining parts of the fatty acid ester, and is recirculated to the first esterification step. The product is a food grade pure ester with over 99% purity.

Purification of glycerol

US 6,015,440 uses flashing and US 5,116,546 uses distillation for removing excess methanol. The methanol is recirculated back for transesterification, whereas the remainder of the glycerol-rich fraction is fed to a conventional fat-splitting operation.

As mentioned earlier, US 5,424,467 uses purified glycerol as the extraction solvent for the ester purification. The pure glycerol can be produced by triple distillation: initially by using an extractive distillation column to separate unreacted alcohol, secondly by using a dewatering column to vaporize water, and thirdly by using a vacuum distillation column where the glycerol is vaporized and separated from the catalyst.

The patent literature is used as guidance in the design and development of our own fuel additive technology.

2. Project Objective

The objective of this project is to create an economical, efficient, and continuous process for producing fuel lubricity additives from locally available vegetable oils resources, and to test the derivatives thus produced for their qualities as fuel lubricity additives.

3. Achievements (papers, presentations)

Following papers, presentations, and graduate student thesis were accomplished based on the work of the present project:

Papers:

1. Munson, J.W., Hertz, P.B., Dalai, A.K., Reaney, M.J., "Lubricity survey of low-level biodiesel fuel additives using the 'Munson ROCLE' bench test", SAE Technical Paper 1999-01-3590, 1999.
2. Munson, J.W., Hertz, P.B., "Survey of seasonal diesel fuel lubricity using the 'Munson-ROCLE' bench test", CANCAM 99 Proceedings, p387, McMaster University, June 1999.
3. Lang, X., Dalai, A.K., Bakhshi, N.N., Reaney, M.J., Hertz, P.B., "Biodiesel esters as lubricity additives: Effects of process variables and evaluation of low temperature properties", Fuels International, 2001 (In Press).
4. Lang, X., Dalai, A.K., Bakhshi, N.N., Reaney, M.J., Hertz, P.B., "Preparation and characterization of biodiesels from various biooil", Submitted for publication in Bioresource Technology.

Conference Presentations:

1. Lang, X., Dalai, A.K., Bakhshi, N.N., Reaney, M.J, "Preparation and characterization of biodiesels from various vegetable oils", Paper 374, 49th Canadian Chemical Engineering Conference, Saskatoon, October 1999.
2. Munson, J.W., Hertz, P.B., Dalai, A.K., Reaney, M.J., "Low-level biodiesel fuel additive survey using the "Munson–ROCLE" bench test", Paper 416, 49th Canadian Chemical Engineering Conference, Saskatoon, October 1999.

Thesis:

1. Munson, J.W., "Development of a precision diesel fuel lubricity bench test – The M–ROCLE", University of Saskatchewan, M.Sc. Thesis, 1999.

4. Results and Discussion

Our earlier results have been reported in the three Interim Reports submitted to ADF. For completion, all the results obtained over the two-year period of this project are included in this Final Report, and are divided into four tasks: (1) Biodiesel ester preparation; (2) Biodiesel ester characterization; (3) Lubricity evaluation; and (4) Process development and economic analyses.

4.1. Biodiesel Ester Preparation

Each vegetable oil has its own distinct fatty acid composition. When it reacts with different alcohols, esters with unique lubricity properties can be formed. In this project, four types of vegetable oils namely, canola, rapeseed, linseed (flax) and sunflower oils, were reacted with methanol, ethanol, 2-propanol (iso-propanol) and butanol to produce various monoesters of the oils (biodiesel). The esters in this report were named according to their oil source and to the alkyl group in the alcohol. For instance, an ester formed by reacting canola oil with methanol was called canola methyl ester (often abbreviated as CME); an ester formed by reacting linseed oil with butanol became linseed butyl ester (or LBE), and so far so forth. In this section, the detailed conditions and procedure for the preparation of these esters are reported

4.1.1. Materials

Rapeseed was purchased from the Saskatchewan Wheat Pool's local supply outlet. The raw edible linseed (flaxseed) was purchased from Early's Farm and Garden, Saskatoon, SK. The rapeseed and linseed oils were expelled from raw seeds using a

small screw press at the Food Science Pilot Plant, University of Saskatchewan, and without further treatment was filtered before transesterification. Degummed, refined canola and sunflower oils (Sunfresh Limited, Toronto, Ont.) were purchased locally. OmniSolv grade methanol (99.9%, BDH Inc., Toronto, Ont.), anhydrous ethanol (Commercial Alcohols Inc., Brampton, Ont.), anhydrous 2-propanol and 1-butanol (both from Aldrich Chemical Ltd.) were used for transesterification reactions. All other reagents were analytical or higher grade.

4.1.2. Methyl esters synthesis

Different reaction conditions and washing methods were experimented with before a successful procedure was developed for the preparation of methyl ester. In the following paragraphs, a detailed preparation procedure was presented using canola methyl ester as an example, as CME was the first ester that was prepared in this project. The other three methyl esters were prepared by following a similar recipe, and thereby were discussed more briefly.

Transesterification

A two-step transesterification process was adopted, which produced an ester that was substantially free of glycerides. First, 200 g of canola oil was added to a clean and dry Erlenmeyer flask. Dryness was absolutely essential as any water in the system would slow the transesterification reaction and consume some of the catalyst. A mass of 23.8 g of methanol (corresponding to the stoichiometry amount) was weighed in a small Erlenmeyer flask. One half gram of sodium methoxide (or 1.0 g of potassium hydroxide) was added as the catalyst into this flask. The mixture was stirred thoroughly until the catalyst was completely dissolved in the methanol. Then, the catalyst-containing

methanol was poured into the oil flask and the mixture was stirred vigorously for 20 minutes at ambient temperature. After the reaction, the content of the flask was transferred into a dry separatory funnel. The dense glycerol settled at the bottom of the funnel and formed a continuous phase. The glycerol phase was typically darker than the original oil and translucent, while the top methyl ester phase was usually lighter in color and slightly cloudy. After settling overnight, the glycerol layer was drawn off the bottom of the funnel and weighed, and the top ester phase was collected into the Erlenmeyer flask. Another 23.8 g of methanol with catalyst was then added to the ester phase, and the previous procedure was repeated for the "second step" of the transesterification. The entire process utilized 100% stoichiometric excess methanol (i.e., the molar ratio of alcohol to oil was 6:1); and 0.5 (for CH_3ONa) or 1.0 (for KOH) wt% of catalyst based on the amount of oil.

Washing

After glycerol was removed by gravity settling, some alcohol and catalyst remained to be dissolved in the crude ester phase, along with traces of soap. Washing the ester phase with water can remove these impurities.

Several washing methods had been tested. The most effective way was found to be the combination of separatory funnel washing followed by column washing. By this procedure, the ester phase was first washed two or three times in a separatory funnel to remove most of the alcohol and soap. After these initial washings, the ester solution was placed in an one-inch diameter washing column on top of a layer of water. An atomization head was then turned on, and the circulating water droplets washed the esters. Washing was continued until the ester phase became completely translucent. The

esters were then removed from the column and washed three more times using distilled water. Significant amount of water, at least 5 times of the volume of the ester were consumed in this process.

Drying

After the canola methyl ester was clear, it was further washed with brine to extract the remaining traces of water from the ester. Next, the ester was filtered through a layer of sodium sulfate by putting the sodium sulfate crystals in a vacuum filtration flask and allowing the oil to be well exposed to the crystals. The dried canola methyl ester was finally bottled and ready for analysis and lubricity testing.

Canola methyl ester: Following this procedure, two canola methyl ester (abbreviated as CME) samples were prepared using two types of alkali catalysts. In the first sample, for 200 g of canola oil, 47.6 g of methanol and 2 g of KOH catalyst as the starting material, 37.0 g of glycerol were removed and 185 g of purified, dry methyl ester were obtained as the final product. The ester yield relative to the theoretical yield was 92%. In the second sample with CH_3ONa catalyst, the CME yield was 97% using the same oil and methanol feedstock.

Other methyl esters: Rapeseed methyl ester (abbreviated as RME), linseed methyl ester (LME) and sunflower methyl ester (SME) were prepared using both potassium hydroxide (KOH) and sodium methoxide (CH_3ONa) as catalysts, following the similar steps as those for the synthesis of canola methyl ester (CME). Briefly, a sample of 200 g of oil (0.226 mole) was placed in a dry flask equipped with a magnetic stirrer and thermometer. In another flask, 23.8 g (0.743 mole) of methanol was mixed with 1.0 g of KOH (0.5% by the weight of oil), or 0.5 g of CH_3ONa until all of the catalyst was dissolved. This

mixture was added to the oil and stirred continuously for 20 minutes at 25°C. After separation of glycerol in a separatory funnel, the ester layer was poured into another flask and transesterified a second time using the same protocol as the first reaction. After the second transesterification, the crude ester was separated again from glycerol and washed with distilled water to remove the catalyst and unreacted methanol. Finally, the ester was dried with anhydrous sodium sulfate. The laboratory scale process yielded 176 – 199 g of methyl esters from 200 g of vegetable oil.

4.1.2. Ethyl ester synthesis

Using CH_3ONa catalyst

The ethyl esters of canola, rapeseed, linseed (flax) and sunflower oil, (abbreviated as CEE, REE, LEE and SEE, respectively), were prepared in much the same way as methyl esters using sodium methoxide (CH_3ONa) catalyst. The transesterification was conducted at 70°C for 2 h with vigorous agitation in order to achieve full conversion. As the ethyl esters tended to form emulsions with water, warm (~50°C) salty (NaCl) water was used as a substitute to reduce emulsification. Tannic acid in water (0.1 wt%) was also an effective washing solution. With mild agitation in a flask, the alcohol and most of the soap could be removed by three washes at 50°C by either solution. After washing, the ethyl esters are dried over anhydrous sodium sulfate.

Sodium methoxide absorbs moisture easily during handling in open air and its vapors are poisonous. When absorbing moisture, the methoxide gradually decomposes into sodium hydroxide and loses catalytic activity.

Using KOH catalyst

Potassium hydroxide is less expensive than CH_3ONa as a base catalyst, but is less

effective for ethyl ester synthesis than for methyl ester preparation. Canola ethyl ester was prepared by reaction at 70°C for 2-3 h, 0.75 or 1.3% KOH catalyst by the weight of oil with different molar ratios of ethanol/oil of 3:1, 5:1 and 12:1. No glycerol layer was observed after reaction under any of these conditions. The low activity observed may be due to a trace of water present in the oil and/or alcohol which may hinder the transesterification reaction.

Using metal sodium (Na) catalyst

The active catalytic species for the triglyceride transesterification is an RO^-, alkoxide anion (R = alkyl group), which can be formed *in situ* by reacting metal sodium or potassium with anhydrous alcohol. In a two-step transesterification process, we have also employed metallic sodium dissolved in anhydrous ethanol as the catalyst for canola ethyl ester production. For each step, 170 mg of metal sodium was freshly cut into small pieces from a sodium block and carefully dropped into 23.5 g (0.51 mole) of ethanol. After the sodium dissolved, the solution was poured into a flask containing 100 g (0.113 mole) of canola oil preheated to 60°C. This procedure resulted in a 4.5:1 molar ratio of ethanol/oil and the equivalent of 0.5% of fresh sodium ethoxide (C_2H_5ONa) per weight of oil. The mixture was vigorously stirred for 2 h at 60°C. After stirring, glycerol separation occurred in the separatory funnel. The top crude ester layer was then subjected to a second transesterification reaction. Significant amounts of soap were formed after the second reaction but these were removed by repeated washing with brine or distilled water and centrifugation. The washed ester was dried over anhydrous sodium sulfate. About 60 g of canola ethyl ester was prepared from 100 g of canola oil. Most losses occurred during repeated washing and separation steps.

4.1.3. Butyl ester synthesis

Using KOH catalyst

Since KOH was cheap and easy to handle, it was first selected as the catalyst for the preparation of butyl esters. Approximately 0.5 g KOH was added into 25.2 g warm butanol, and was dissolved in 5 min. The catalyst solution was then poured into 50 g of canola oil preheated at 70°C, under vigorous stirring. The amount of chemicals gave a molar ratio of butanol to oil of 6:1 (100% excess of butanol from the stoichiometry) and 1% KOH catalyst by the weight of oil. The reaction lasted for 2.5 h at 70°C with continued agitation. At the end of the reaction, the content was transferred to a separatory funnel. After overnight settling, no phase separation of glycerol from crude ester was observed. It was interpreted that the transesterification to butyl ester was not successful by using KOH as a catalyst.

Using metal sodium (Na) catalyst

Canola butyl ester: Canola butyl ester (CBE) was then prepared using metal Na as the catalyst (or catalyst precursor), following the same two-step procedure as that used for its ethyl ester (CEE). In the first step, 170 mg of metal sodium was freshly cut into small pieces from a sodium block and carefully dropped into 37.5 g of butanol. After the sodium was dissolved, the solution was poured into a flask containing 100 g of canola oil preheated to 65°C. It may be noted that with 100 g of canola oil 170 mg of metal Na was used for CBE as in case of CEE preparation. Therefore, the mol% of sodium butoxide used for CBE was the same as that of sodium ethoxide used for CEE. It may also be noted that the wt% of the two sodium alkoxides was different in their respective preparations due to the difference in the molecular weights between ethoxide and

butoxide. The molar ratio of butanol to oil was also maintained at 4.5:1 (50% excess of the stoichiometry) for this step. The mixture was vigorously stirred for 2 h at 65°C. After settling overnight, about 2 g of glycerol was withdrawn from the bottom of a separatory funnel. This showed that metal Na was effective as a catalyst for the transesterification between canola oil and butanol. The top crude ester layer was then returned to the reaction flask for the second step of transesterification. Another 170 mg of metal Na was dissolved in a fresh 37.5 g of butanol and added to the flask. The second step was carried out at 60°C overnight with continued stirring. However, no more glycerol was separated after the second reaction. The crude ester was washed with about 100 ml brine or distilled water each time in a separatory funnel for several times. After settling, most of the water was drained from the funnel bottom. The top layer, often an emulsion, was divided into small tubes and transferred to a centrifuge for further separation. Washing was repeated until no more soap was formed and the pH of the drained water became 7. After that, the ester was dried over anhydrous sodium sulfate. Finally, about 75 g of CBE was collected from 100 g of canola oil. The low yield was the result of incomplete conversion during transesterification and losses occurred during repeated washing and separation steps. Since the second transesterification at 60°C did not improve the yield, it was decided to use one-step but at a higher temperature in the next butyl ester preparation.

Linseed butyl ester: The one-step preparation of linseed butyl ester (LBE) was the following: 170 mg metal Na chips were first dissolved in 50.8 g of butanol. The sodium butoxide/butanol was then poured into 100 g of linseed oil preheated at 105°C (the boiling point of butanol is 117.7°C). The butanol to oil molar ratio was 6:1. The reaction

lasted for 3 h at 100°C with vigorous agitation. The oil color turned to brown immediately after butoxide/butanol was poured in. This may indicate that glycerol was formed very quickly. After phase separation, about 11 g of glycerol was withdrawn from the bottom of the separatory funnel. The crude ester was then washed with brine or distilled water by the same technique as that used for CBE, and dried over anhydrous sodium sulfate. Finally, 106.6 g of LBE was collected from 100 g of linseed oil. This was a significant improvement from the CBE preparation, and reached 96% of the theoretical yield.

4.1.4. 2-Propyl Ester Synthesis

Using KOH catalyst

KOH was also first tested as the catalyst for the preparation of 2-propyl esters. About 0.5 g of KOH was dissolved in 20.3 g of 2-propanol before being added to 50 g of canola oil. The reaction continued for 2.5 h at 75°C with vigorous stirring. After overnight settling, no glycerol, but soap, was found at the bottom of the funnel. Therefore, it was concluded that KOH was also ineffective for 2-propyl ester synthesis.

Using metal sodium (Na) catalyst

Metal Na was used as the catalyst for the preparation of canola 2-propyl ester (CPE) and linseed 2-propyl ester (LPE), respectively. The conditions for the one-step reaction were similar to that for LBE as described earlier, except the reaction temperature was at 70°C (the boiling point of 2-propanol is 82.4°C). For CPE, 170 mg of metal Na chips were dissolved in 40.6 g of 2-propanol. Then the solution was mixed with 100 g canola oil. For LPE, 170 mg Na and 41.2 g of 2-propanol were used for 100 g of linseed oil. Therefore, the same mol% of sodium alkoxide catalyst and the same alcohol to oil

molar ratio of 6:1 was used in the ethyl, butyl and 2-propyl ester preparations when using metal Na as catalyst. After washing and drying, 96 g of CBE and 90 g of LBE were collected. However, after storage on the shelf for a few days, the original clear esters became somewhat foggy. Monoglyceride impurity in these samples may have caused turbidity in the esters.

In total, 12 different biodiesel esters were prepared, which included four methyl esters and four ethyl esters of canola, rapeseed, linseed and sunflower oils, as well as two butyl esters and two 2-propyl esters of canola and linseed oils. These esters differed greatly in their compositions, and thus provided a sufficiently large sampling pool from which a candidate ester could be selected as an effective fuel lubricity additive.

4.2. Biodiesel Ester Characterization

The second major task of the project was the characterization of the esters that had been prepared. The data collected from the characterization studies allowed the comparison of the properties of the esters with those of conventional diesel fuels, and thereby to assess their compatibilities when biodiesel esters were blended into diesels as fuel additives. The chemical compositions of the 12 esters were analyzed by chromatographic methods for both the lipid and fatty acid compositions, and by Inductively Coupled Plasma Spectrometry (ICPS) for the residual Na contents. Basic physical and chemical properties, including density, viscosity, pour point and cloud point, iodine value, acid value, and heat of combustion, were determined following the standard test procedures. Other instrumentation methods such as Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were also applied for the low temperature and volatility studies. The results of the ester characterization are reported in this section, the relevant properties of the source oils and reference diesel fuel samples are also included.

4.2.1. HPLC

The lipid compositions of the transesterification products were determined by High Performance Liquid Chromatography (HPLC) using a Waters GPC-Styragel 0.5 column (7.5 x 30 mm) with tetrahydrofuran as the mobile phase combined with evaporative light scattering detection (ELSD). The column was operated at 35°C while the ELSD detector was at 40°C.

The HPLC method employed was the low molecular weight gel permeation

chromatograph, which separated different components according to their solvated molecular size, with the larger one eluting first. Therefore, any unreacted triglycerides (TGs) will first elute, followed by diglycerides (DGs), monoglycerides (MGs), and finally alkyl esters (biodiesels). The chromatogram of a crude, unwashed CEE sample after its separation from glycerol is shown in Figure 1a. It can be seen that the classes of lipids were efficiently separated and trace residual glycerides were readily detected in the crude esters. The retention times of triglycerides (around 5.6 min), diglycerides (5.9 min) and monoglycerides (6.3 min) and alkyl esters were well resolved. The majority (over 90%) of the fatty acids in the canola, linseed and sunflower oils were those containing 18 carbons and included stearic, oleic, linoleic and linolenic acids in the order of increasing unsaturation. Their alkyl esters emerged as a single peak in the gel permeation chromatogram because of similar molecular sizes. On the other hand, rapeseed oil contained approximately 7% eicosenoic and 54% erucic acids, which were 20 and 22 carbon monounsaturated fatty acids, respectively. Subsequently, the alkyl esters of rapeseed oil yielded two peaks in the chromatogram as shown in Figure 1b, for RME. The earlier and larger one at about 6.5 min represented the bulkier C_{20} and C_{22} fatty acid esters while the later one at 6.8 min was for the esters of the C_{18} fatty acids. All samples of methyl, ethyl and butyl esters exhibited only the ester peaks in the chromatograph, demonstrating the high purity of these samples. Small mono- and diglycerides peaks were detected in the chromatograms of CPE and LPE samples, indicating trace impurities in the 2-propyl esters.

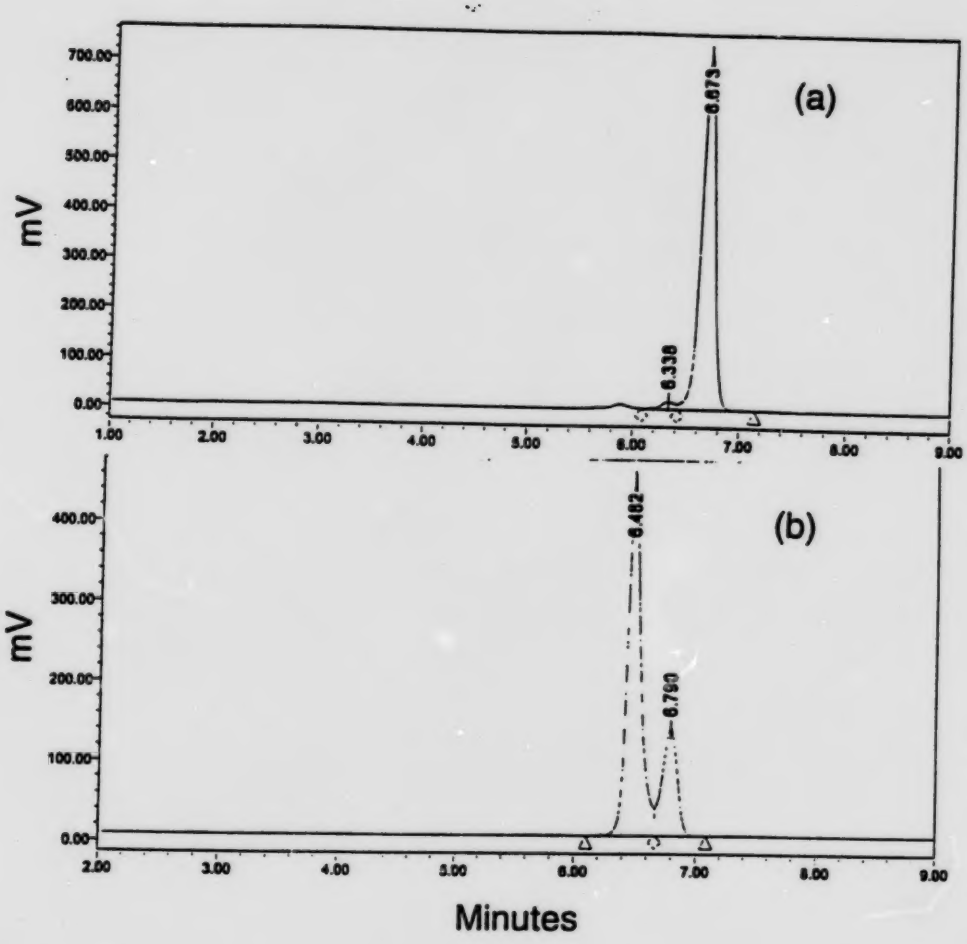

Figure 1. HPLC chromatograms of (a): crude canola ethyl ester and (b): purified rapeseed methyl ester.

4.2.2. Fatty acid composition

Fatty acid compositions of the biodiesel esters were measured by Gas Chromatography (GC) according to the American Oil Chemists Society (AOCS) standard method Ca 5a-40 (28). A Hewlett Packard GC (model 5890) equipped with a DB-FFAP column and flame ionization detector was used for the analysis.

The fatty acid compositions of 12 biodiesel esters are presented in Table 2. A total of 7 different fatty acids were found in the esters. As expected, the different lower alkyl esters originating from the same vegetable oil source had similar fatty acid compositions. The dominant fatty acid in canola oil esters was oleic acid (18:1) averaging at 68 wt%. In the sunflower oil esters it was linoleic acid (18:2) at 68 wt%, and in linseed oil esters it was linolenic acid (18:3) at 62 wt%. These three fatty acids all have an 18 number carbon chain with the number of double bonds increasing from 1 to 3, respectively. Erucic acid (22:1) was the most common fatty acid found in rapeseed oil esters at an average of 54 wt%. All these vegetable oil esters had very high unsaturated fatty acid content, ranging from about 88 % (sunflower esters) to 97 % (rapeseed esters). Palmitic (16:0) and stearic (18:0) were the only two saturated fatty acids, in minor amount, found in these esters.

Table 2. Fatty acid composition (wt%) and calculated iodine values of the esters.

Fatty acid	CME	CEE	CPE	CBE	LME	LEE	LPE	LBE	RME	REE	SME	SEE
Palmitic (16:0)	4.2	4.4	4.5	4.4	5.2	5.1	5.1	5.3	3.1	3.1	6.5	6.3
Stearic (18:0)	2.2	2.3	2.3	2.3	3.2	3.1	3.1	3.2	0.0	0.0	4.9	4.7
Oleic (18:1)	67.2	69.4	67.3	67.8	14.5	13.7	14.2	13.8	13.9	13.2	20.5	21.0
Linoleic (18:2)	18.9	18.0	19.4	18.9	15.3	15.2	15.1	15.2	13.3	13.3	68.0	68.0
Linolenic (18:3)	7.4	5.9	6.5	6.7	61.9	62.9	62.5	62.6	9.4	9.2	0.0	0.0
Eicosenoic (20:1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.8	6.9	0.0	0.0
Erucic (22:1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	53.5	54.4	0.0	0.0
Total saturated	6.4	6.7	6.8	6.7	8.4	8.2	8.2	8.5	3.1	3.1	11.4	11.0
Total unsaturated	93.6	93.3	93.2	93.3	91.6	91.8	91.8	91.5	96.9	96.9	88.6	89.0
Calculated Iodine Value	115.0	111.2	113.5	113.4	210.0	211.7	210.9	211.0	108.0	107.3	141.6	141.9

4.2.3. Density

The densities of the biodiesel esters were determined using a Parr model DMA 35 density meter at 25°C according to the method of ASTM D5002 (29). Reverse osmosis water was used to calibrate the density meter.

The densities of the four pure oils and their 12 biodiesel esters measured at 25°C are presented in Table 3. It was found that the densities of the pure oils were in the range of 0.91 to 0.93 g/ml, and those of the biodiesel esters were reduced to 0.86 to 0.89 g/ml. For the different alkyl esters made from the same source of vegetable oil, the density changed in the order of methyl ~ 2-propyl > ethyl > 1-butyl esters. The density of a typical No 1 Canadian winter diesel fuel (LSD-43 Diesel Light) was 0.82 g/ml, while that of a No 2 summer diesel fuel (C-5 Seasonal Diesel) was 0.86 g/ml (26). Both diesel fuels were not additized, and have been used as reference fuels in the related studies of biodiesel esters as lubricity additives. In comparison, the biodiesel esters averaged 7% and 2% higher specific weights than the No 1 and No 2 diesel fuels, respectively.

Table 3. Density of the vegetable oils and their esters.

	Density at 25°C, (g/ml)				
Oils	Pure oil	Methyl	Ethyl	2-Propyl	Butyl
Linseed	0.925	0.887	0.884	0.888	0.877
Canola	0.912	0.875	0.869	0.874	0.861
Sunflower	0.914	0.882	0.876	n.d.*	n.d.
Rapeseed	0.908	0.877	0.873	n.d.	n.d.

*: n.d.: not determined.

4.2.4. Viscosity

Viscosity of the esters was measured at 40°C using a Brookfield model RVTDCP, cone and plate viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA). A Cannon certified viscosity standard was used to calibrate the viscometer.

The dynamic viscosity at 40°C of the four vegetable oils and their esters are given in Table 4. The viscosity of the pure vegetable oils used in this study ranged from 22.4 cP (linseed oil, 1 cP = 1×10^{-4} Pa-s) to 45.1 cP (rapeseed oil). After transesterification, the viscosity of their lower alkyl esters was reduced to the lowest value of 3.32 cP for LME to the highest viscosity of 7.60 cP for REE. For linseed and canola esters, the viscosity increased as the size of the alkyl group increased from methyl < ethyl < butyl ester. Both 2-propyl esters of linseed and canola oils had higher viscosity, possibly in part due to the glyceride impurities in these two esters. For the same alkyl esters, their differences in viscosity were dependent on those of the vegetable oils. For example, the rapeseed oil was the most viscous one among the four oils; consequently, the viscosities of its methyl and ethyl esters were the highest in their respective series. The viscosities of the No 1 and No 2 diesel fuels were 1.75 and 3.50 cP at 40°C, respectively. In comparison, the biodiesel esters had viscosity 1.9-4.2 times that of No 1 diesel fuel and 0.95-2.2 times that of No 2 diesel fuel.

Table 4. Viscosity of the vegetable oils and their esters.

	Dynamic Viscosity at 40°C (cP)				
Oils	Pure oil	Methyl	Ethyl	2-Propyl	Butyl
Linseed	22.4	3.32	3.64	4.88	4.06
Canola	33.4	3.79	3.91	6.24	4.39
Sunflower	28.9	4.24	4.40	n.d.	n.d.
Rapeseed	45.1	5.18	7.60	n.d.	n.d.

4.2.5. Cloud and pour points

The cloud point of any petroleum fuel oil is defined as the temperature at which a cloud of wax crystals first appears in the oil when it is cooled at a specific rate. The pour point is the lowest temperature at which the oil specimen can still be moved. Both quantities are often used to specify cold temperature usability of fuel oils. The cloud points of the biodiesel esters were determined according to ASTM D2500 method (30), and the pour points of the esters were determined according to the procedures of ASTM D97 (31). Three cooling baths with different cooling temperatures were used. The first bath was maintained at about -5°C by mixing crushed ice and sodium chloride crystals. The second one with -15 to -18°C was made using crushed ice and calcium chloride crystals. Chilling acetone with dry ice furnished the third bath, with temperature down to –35°C.

The cloud point and pour point of various biodiesel esters of the four vegetable oils are shown in Table 5. The cloud points for ethyl esters were approximately 2°C lower than that of the corresponding methyl esters, while butyl esters of linseed and

canola oil were 10 and 7°C lower, respectively, than their methyl esters. The cloud points of the two branched-chain esters were rather high. Cloud formation was observed at the bottom of the test jar at 3°C and 7°C for LPE and CPE, respectively. In preparing the 2-propyl esters for cloud point determination, some crystals were separated from the samples by centrifuging before the measurements. These crystalline materials were shown by HPLC as mono- and diglycerides. Even after such pretreatment, the remaining impurities interfered with the observation, resulting in higher readings of cloud point. When Lee et al. (15) measured the cloud and pour points for different branched-chain esters of soybean oil, they also observed similar interference of monoglyceride impurities with the cloud point of 2-butyl ester. However, they found that these impurities did not interfere with pour point measurement. Among all the biodiesels, CBE had the lowest pour point of –16°C, while SEE had the highest of –5°C. With the eight methyl and ethyl esters, the two rapeseed esters, RME and REE, showed much lower pour point of –15°C in comparison with other ones.

Table 5. Cloud point and pour point of the biodiesels from vegetable oils.

	Cloud Point, (°C)				Pour Point, (°C)			
Oils	Methyl	Ethyl	2-Propyl	Butyl	Methyl	Ethyl	2-Propyl	Butyl
Linseed	0	-2	3	-10	-9	-6	-12	-13
Canola	1	-1	7	-6	-9	-6	-12	-16
Sunflower	1	-1	n.d.	n.d.	-8	-5	n.d.	n.d.
Rapeseed	0	-2	n.d.	n.d.	-15	-15	n.d.	n.d.

The cloud and pour points of the No 1 Canadian winter diesel fuel were –50°C and –51°C, respectively, which were much lower than those of all the biodiesel esters.

The No 2 summer diesel fuel had cloud and pour points of –8 and –15°C, respectively. These summer values were close to the cloud and pour points of LBE and CBE. Using butyl alcohol, the cold flow properties of the biodiesel were improved to the level of the summer diesel fuel. Also, the pour point of RME and REE were comparable to that of the summer diesel fuel.

4.2.6. Acid value

The acid value is defined as the mg of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. Acid values of the biodiesel esters were determined by color-indicator titration following AOCS official method Te 2a-64 (32), especially applicable to fatty alcohols and fatty esters. Since the acid values of the biodiesels are usually less then 1 mg KOH/g, approximately 20 g of ester samples were used for the analysis, and a standardized 0.056 N NaOH solution was prepared for the titration.

The acid values of various biodiesel esters are listed in Table 6. Their numbers varied from low 0.15-0.16 mg KOH/g for REE and CME to highest 0.61 for SEE. Conventional diesel fuel possessed a very low acid value of 0.002.

Table 6. Acid value of the biodiesel esters.

	Acid Value, (mg KOH/g)			
Oils	Methyl	Ethyl	2-Propyl	Butyl
Linseed	0.335	0.324	0.586	0.254
Canola	0.163	0.265	0.469	0.280
Sunflower	0.179	0.610	n.d.	n.d.
Rapeseed	0.430	0.152	n.d.	n.d.

The suggested ASTM standard for pure biodiesel sets the maximum acid value (acid number) at 0.8 mg KOH/g while the German standard DIN V 51606 sets it at 0.5 mg KOH/g (3).

4.2.7. Calculated iodine value

The iodine value (IV) describes the unsaturation of oils and their fatty acid derivatives, and is expressed as grams of iodine absorbed/100 g sample under standard conditions. Although the iodine value is often determined by the Wijs titration method such as AOCS method Cd 1-25 (33), it uses a toxic solvent for the analysis. In this study, the iodine value was directly calculated based on the known fatty acid composition (FA%) in the esters and corresponding acid factors (AF). AFs are the reacting ratios of I_2 to the individual fatty acids.

$$IV = \sum(AF * FA\%).$$

The AOCS Recommended Practice Cd 1c-85 (34) has listed acid factors for several common free fatty acids found in edible oils. The acid factors are 0.9976 for palmitoleic acid, 0.8986 for oleic acid, 1.810 for linoleic acid, 2.735 for linolenic acid, 0.8175 for eicosenoic acid and 0.7497 for erucic acid. Using these factors, the iodine values of the biodiesels were calculated and shown in Table 1. Since the iodine values was only depended on the origin of the vegetable oil, the biodiesel esters made from the same oil showed similar iodine values. The average iodine values were 108, 113, 142, and 211 for rapeseed, canola, sunflower and linseed esters, respectively, in the order of their increasing unsaturation. The linseed esters had the highest iodine value because its major constituency was linolenic acid, a triple double-bond fatty acid. The iodine value of the conventional diesel fuel was approximately 10 (10). Therefore, the biodiesels had

significantly higher degree of unsaturation than diesel fuel. When heating unsaturated fatty acids, polymerization of glycerides will occur, which may lead to gum formation. This problem could be worse with the number of double bonds in the fatty acid chain increased. To ensure the quality of biodiesel as alternative fuel, Mittelbach (35) proposed to limit the unsaturated fatty acid in biodiesel specifications, especially the content of higher unsaturated fatty acids, like linolenic acid.

4.2.8. Heat of combustion

Gross heat of combustion of the biodiesel esters and the four pure vegetable oil samples were determined following ASTM D240 (36), using a Parr model 1341 oxygen bomb calorimeter with an isothermal jacket. Approximately 50 wt% of primary standard benzoic acid powder, used as a combustion aid, was mixed with sample liquids in the crucible to ensure complete combustion after firing.

Heat of combustion measures the energy content in a fuel. It is an important property of the biodiesels that determines the suitability of these materials as alternative to diesel fuels. The gross heat of combustion of the 4 pure vegetable oils and the corresponding 12 esters are listed in Table 7. The values of the gross heat of combustion ranged from 39.56 (CPE) to 40.97 MJ/kg (REE) for various esters. These values were the same or slightly higher than those of the pure vegetable oils. The heat content of the diesel fuel was approximately 45 MJ/kg. The vegetable oil and their esters contained approximately 11% less heat energy on a mass basis. Since the density of the biodiesel esters were 2 to 7% higher than that of diesel fuels, the heat energy of the biodiesels therefore was about 9 to 4% lower on a volume basis.

Table 7. Gross heat of combustion of the vegetable oils and their esters.

	H_g, (MJ/kg)				
Oils	Pure oil	Methyl	Ethyl	2-Propyl	Butyl
Linseed	39.51	40.00	39.65	39.56	40.38
Canola	39.78	40.07	40.41	40.04	40.24
Sunflower	39.46	39.71	39.80	n.d.	n.d.
Rapeseed	40.27	40.43	40.97	n.d.	n.d.

4.2.9. Thermogravimetric analysis (TGA)

The TGA technique has been employed to yield information on the volatility of the biodiesels since the volatility influences the ignition quality of the fuels in a compression ignition engine. The weight loss of the biodiesel esters with respect to temperature was measured using a Mettler TA4000 desktop thermal analysis system with a TG50 thermobalance. In the study, about 10 mg of sample was placed in an aluminum pan and heated at 5°C/min ramp rate from 30 to 350°C in 50 ml/min nitrogen purge gas. A separate blank run was conducted using the empty pan under identical conditions, and the data were used for baseline correction during the evaluation of the sample TGA profiles.

A typical TGA profile of biodiesel esters (CME), along with that of the two reference diesel fuel samples, is shown in Figure 2. The No 1 winter diesel fuel was very volatile even at room temperature. Its 5% distillation temperature, which is an indication of the potential onset of combustion, was 54.7°C (see Table 8). It rapidly evaporated when heated to 70°C and completely volatilized at approximately 135°C (Figure 2). The No 2 summer diesel fuel was twice more viscous than the No 1 diesel fuel, thus it

vaporized more slowly and lost 95% of its initial weight after being heated to 220°C. The onset of volatilization and distillation temperatures estimated from the TGA data for the 12 biodiesel esters and the two diesel fuels are presented in Table 8. The biodiesel esters were considerably less volatile in comparison to the diesel fuels. Taking CME as an example, it showed negligible weight loss when heated below 150°C. It only began rapid evaporation around 180°C. At 250°C, the volatile components in the CME, which accounted for approximately 90% of the weight, had been lost (see Figure 2 and Table 8). The remaining 10% were much more viscous and a portion of it stayed in the pan until 350°C. The residue was completely burnt after heating to 800°C while cleaning the pan. The TGA curves of other esters were similar to that of CME as shown in Figure 2, with varying onset and distillation temperatures depending on the composition of the esters. For different esters from the same vegetable oil, methyl esters were the most volatile ones. The volatility decreased as the alkyl group grew bulkier. The high content of long chain unsaturated fatty acids in the biodiesel contributed to its poor volatility and tendency to form deposits at high temperature. On the positive side, less volatility means less flammability; biodiesel esters would be safer in transportation and storage compared to conventional diesels.

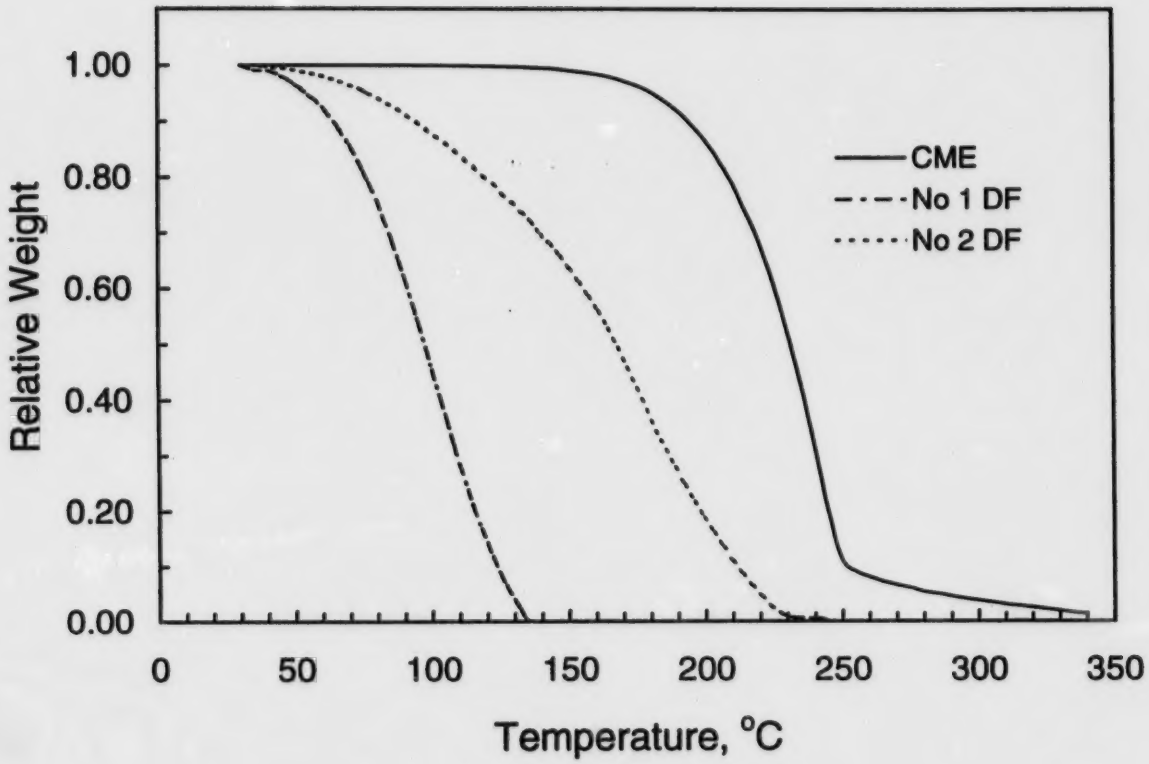

Figure 2. TGA curves of the canola methyl ester and the reference diesel fuels.

Table 8. Volatilization and distillation temperatures from the TG analysis.

Samples	Onset of Volatilization (°C)[a]	Distillation Temperature (°C)		
		10%	50%	90%
CME	181.1	194.1	231.5	251.7
CEE	182.3	197.1	237.5	264.7
CPE	190.5	206.6	247.4	328.4
CBE	149.2	197.8	251.1	285.0
LME	176.1	188.8	229.5	246.7
LEE	178.4	191.9	231.7	298.6
LPE	178.7	192.6	234.6	326.1
LBE	173.2	197.1	249.6	332.8
SME	178.2	192.9	236.1	>350
SEE	187.3	202.3	247.3	320.3
RME	192.7	206.9	251.8	293.6
REE	203.2	220.5	274.4	>350
No 1 winter DF	54.7	64.0	97.3	123.5
No 2 summer DF	76.8	94.1	168.3	211.4

[a]At 5% weight loss.

4.2.10. Differential Scanning Calorimetry

In addition to the cloud point and pour point measurements, the Differential Scanning Calorimetry (DSC) method was also applied to study the low temperature properties of the biodiesel esters.

The differential scanning calorimeter used was a TA Instrument, DSC 2010 with a TA 2100 PC-based controller to record and analyze the cooling and heating thermograms. In each scan, approximately 10 mg of an ester sample was weighed and was hermetically sealed in an aluminum pan. An empty pan was used as a reference. Samples were first equilibrated at 30°C before cooling at 5.0°C/min to –60°C, and then held isothermally at –60°C for 5 min before heating to 30°C at 5.0°C/min. Canola 2-propyl and butyl esters as well as the sunflower esters were cooled to –75°C. Each ester was scanned in triplicate, each time with a fresh sample. Both cooling and heating curves were analyzed for freezing and melting points of the esters as well as the latent heats associated with the transitional processes.

Typical DSC thermograms of the four vegetable oil esters are shown in Figures 3a-d. For canola ester (Figure 3a), two peaks were detected in the cooling curve (top). The first peak, small and broad over about 30°C range, represented the transition from liquid to solid of minor saturated fatty acid esters (e.g., palmitic and stearic esters). The second peak occurred at much lower temperature and was large and sharp. It was responsible for the transition of the major components, the mixtures of unsaturated fatty esters. This pattern was similar to the DSC thermogram of a known 11:4:25 palmitic/stearic/oleic ester mixture obtained by Lee et al. (15). In the heating curve

(bottom, read from left to right), the peak sequence was reversed, and additional minor transitional peaks were detected probably because of polymorphism of the fatty acid during its melting (37). The DSC thermograms of sunflower esters were similar to those of the canola esters, except the major peak appeared at much lower temperature (Figure 3b). Only small peaks at around –20°C with low heat of transition values were found for linseed esters (Figure 3c). The primary fatty acid of the linseed oil/ester is linolenic acid, and the melting point of linolenic methyl ester is –57°C (38). Since the melting point of a mixture is generally lower than those of its individual components, it seems that the major transitional peak of linseed ester was not detected in our DSC scan even when cooled down to –75°C. The cooling curve of the rapeseed esters also had two peaks (Figure 3d), with the first peak as the bigger one, representing its primary 22 carbon-chain erucic acid ester.

Table 9 summarizes the major peak temperatures of the biodiesel esters as well as the heat associated with the transition, from both the cooling and heating curves obtained during the DSC analysis. The values were averaged from three scans. The freezing temperature of an ester was always lower than its melting temperature, because the freezing, or crystallization, was dependent on the kinetics of nucleation while the melting was a thermodynamic process. The heat of transition was about 50-70 kJ/kg. The very low value of 16 kJ/kg for the sunflower ethyl ester probably was an artifact, as its freezing transition may not be completed at the end of the scan. Data for linseed esters were not available, since their freezing and melting peaks were likely below –75°C, which was beyond the scanning range of the DSC performed.

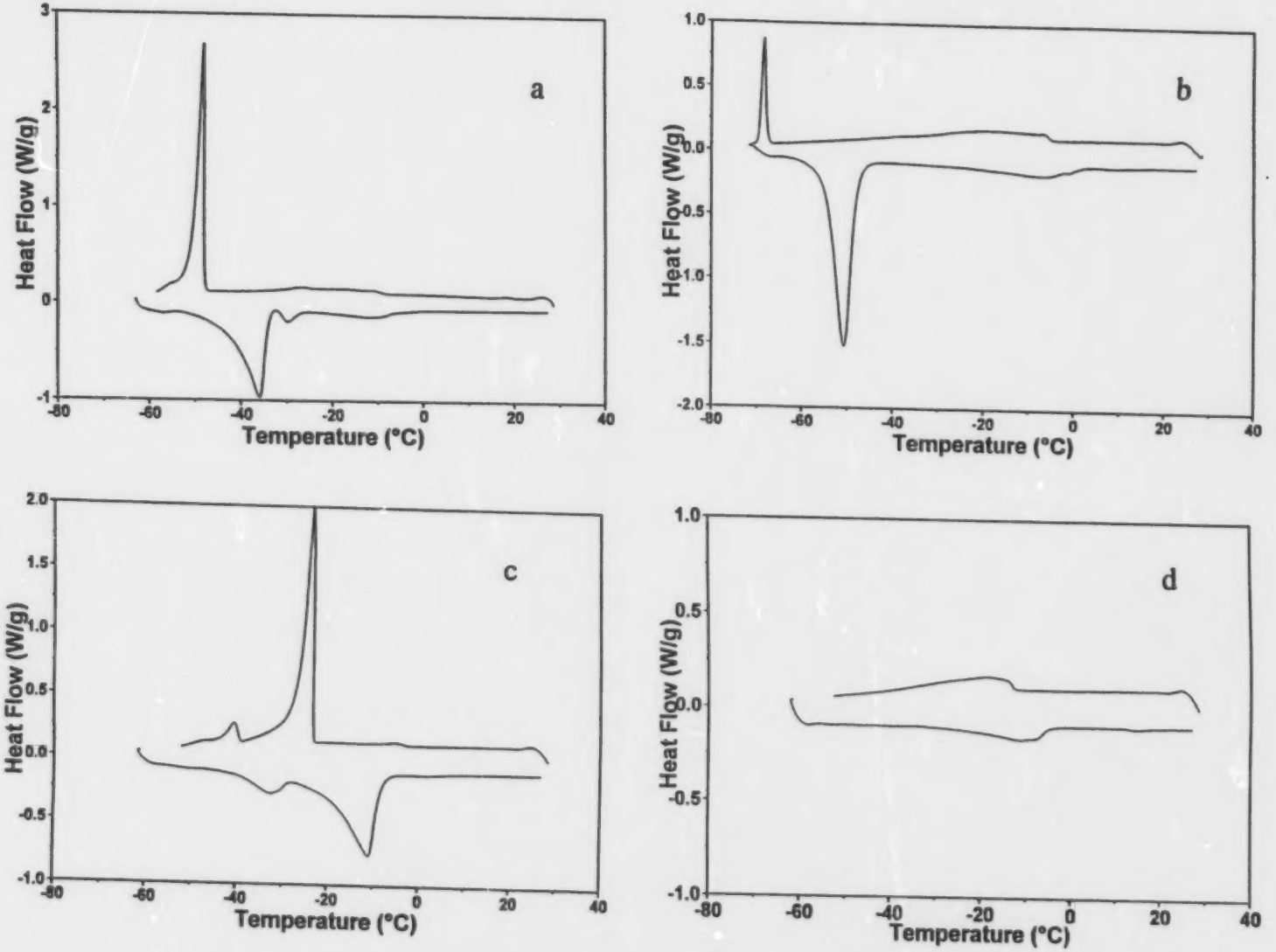

Figure 3. Typical DSC thermograms of (a): canola ester, (b): sunflower ester, (c): linseed ester and (d): rapeseed ester (top branch: cooling curve, bottom branch: heating curve).

Table 9. The peak temperature (°C) and the related heat of transition (kJ/kg, in parentheses) of the biodiesel esters measured by DSC.

Oil source	Esters			
	Methyl	Ethyl	2-Propyl	Butyl
		Freezing		
Rapeseed	-22.5 (61.4)	-34.5 (53.7)	-	-
Canola	-48.5 (60.2)	-52.0 (66.9)	-66.0 (31.4)	-57.4 (48.0)
Sunflower	-68.8 (69.4)	-71.1 (15.8?)	-	-
Linseed	NA*	NA	NA	NA
		Melting		
Rapeseed	-10.9 (60.9)	-25.7 (61.2)	-	-
Canola	-36.1 (58.5)	-29.3 (61.3)	-52.0 (39.6)	-48.1 (52.2)
Sunflower	-50.8 (74.7)	-45.8? (17.6?)	-	-
Linseed	NA	NA	NA	NA

*NA: not available.

The transitional peak temperatures (both freezing and melting) of the methyl esters and ethyl esters decreased in the sequence of rapeseed > canola > sunflower (> linseed). For example, the melting peak temperatures of the methyl esters were –10.9, –36.1 and –50.8°C for RME, CME and SME, respectively and that of LME would be even lower. In general, the melting point of linear, long-chain fatty acids and their esters decreased as the carbon chain length decreased if the number of double bonds was the same, and as the number of double bonds increased if the chain length was the same. The primary fatty acids of the rapeseed, canola, sunflower and linseed oil/esters were, respectively, erucic (22:1), oleic (18:1), linoleic (18:2) and linolenic (18:3) acid (Table 2), and their melting points were 33, 16, -5, -11°C, respectively. Therefore, for biodiesel

esters having the same alkyl tail group, the rapeseed esters should show the highest transitional peak temperatures, whereas linseed esters should have the lowest ones among these four different vegetable oil esters.

Replacing lower alkyl tail group from methyl to ethyl to butyl, the transition peak temperatures of the canola esters also progressively decreased. For example, the freezing peak temperature went from –49°C for CME to –52°C for CEE and down to –57°C for CBE. Freezing, the transition from liquid to solid, involves the arrangement of molecules in an orderly form. When a bulkier tail group is introduced into a linear, long-chain ester, it seems to disturb intra-molecular association thus reducing freezing temperature (37). Replacing the straight chain alkyl group with a branched chain moiety, 2-propyl, in the canola ester further reduced its freezing peak temperature to –66°C. This finding was in agreement of other studies in the literature. Lee et al. (15) reported that the onset temperature from the DSC melting curve of soybean 2-propyl ester was lower by 5.5°C in comparison to its 2-propyl ester.

4.2.11. Sodium residual analysis

The allowable sodium residual level is not specified in either ASTM standard or European standards for biodiesel. However, based on the group's previous experience, a high Na level in a biodiesel fuel blend may cause engine failure. When a diesel engine was run with a fuel blended with 30% biodiesel that contained approximately 4 ppm Na, the engine began mis-firing after about 15 hours. In comparison, the same engine lasted indefinitely when run with a 10% biodiesel blend and the biodiesel in the blend contained 0.2 ppm Na.

The residual sodium (Na) levels in the biodiesel esters were analyzed by Inductively Coupled Plasma (ICP), performed by the Fluid Life Corp. (Edmonton, AB). The ICP results are given in Table 10 for total of 15 samples. Two samples of LME, RME and SME were listed in the table, each prepared by using a different catalyst (NaOH vs. KOH). Also included were two "unpurified" CEE samples that had undergone different stages of washing.

Table 10. Sodium residual level in the biodiesel esters measured by ICP.

Ester	Catalyst for Synthesis	Na (ppm)
CME	NaOH, KOH	3.0
LME	NaOH	3.6
LME	KOH	1.5
RME	NaOH	0.9
RME	KOH	3.0
SME	KOH	2.4
SME	NaOH	3.0
CEE	Na metal	2.7
LEE	Na metal	13.8
REE	CH_3ONa	904.2
SEE	CH_3ONa	293.1
CPE	Na metal	149.2
LPE	Na metal	31.5
CBE	Na metal	19.6
LBE	Na metal	9.0
CEE-crude	Na metal	673
CEE-5w	Na metal	154

All biodiesel samples, except one (RME using NaOH catalyst), had sodium residual over 1 ppm. The three methyl esters prepared using KOH catalyst were also found to contain sodium from 1.5 to 3.0 ppm, which were similar to their counterparts prepared using NaOH catalyst. The ester samples synthesized using metal sodium as the catalyst generally had higher residual sodium. The REE and SEE showed very high sodium levels up to 900 and 300 ppm, respectively.

The crude CEE (CEE-crude), just after separation from glycerol, was found to contain 673 ppm of sodium. After five washings with distilled water (CEE-5w), the sodium decreased to 155 ppm. It eventually reduced to 2.7 ppm in the final sample after more washing. Therefore, the sodium residual level apparently depended on how effectiveness the washing was done. The researchers at AFFC, Saskatoon Research Center previously had used a diluted acidic solution for biodiesel washing, and often achieved "ultra" pure biodiesels with Na level below 0.5 ppm.

The ICP sodium data raised a few questions that needed to be answered. For instance, how did the non-sodium (KOH) catalyzed esters also contain a few ppm of sodium? Background checks on the source vegetable oils for sodium may be required as a quality control item during the ester processing. Also, high sodium (>100 ppm) levels in the ester can cause significant soap formation which has to be reduced; but what will be the acceptable Na level for a "no-harm" engine performance? For the safe use of biodiesel as fuel additives, further study on sodium residuals on engine performance is evidently warranted.

4.3. Lubricity Evaluation

While the work on chemical, physical characterization were performed in the Department of Chemical Engineering and at AAFC, lubricity tests of the biodiesel esters were carried out in parallel in the Department of Mechanical Engineering, University of Saskatchewan. In this section, the improvement made on the M-ROCLE tribology testing machine was first described, followed by the discussion of the lubricity data obtained from the M-ROCLE tests, and then the statistical analyses of the data. The section is concluded with a recommendation of the best candidate for a biodiesel ester lubricity additive.

4.3.1. M-ROCLE lubricity test machine

A Munson Roller on Cylinder Lubricity Evaluator (M-ROCLE) was developed in the Department of Mechanical Engineering during the project, for the determination of the tribological performance of biodiesel esters as diesel fuel additives. The schematics of the M-ROCLE test machine is shown in Figure 4, and the test conditions are given in Table 11.

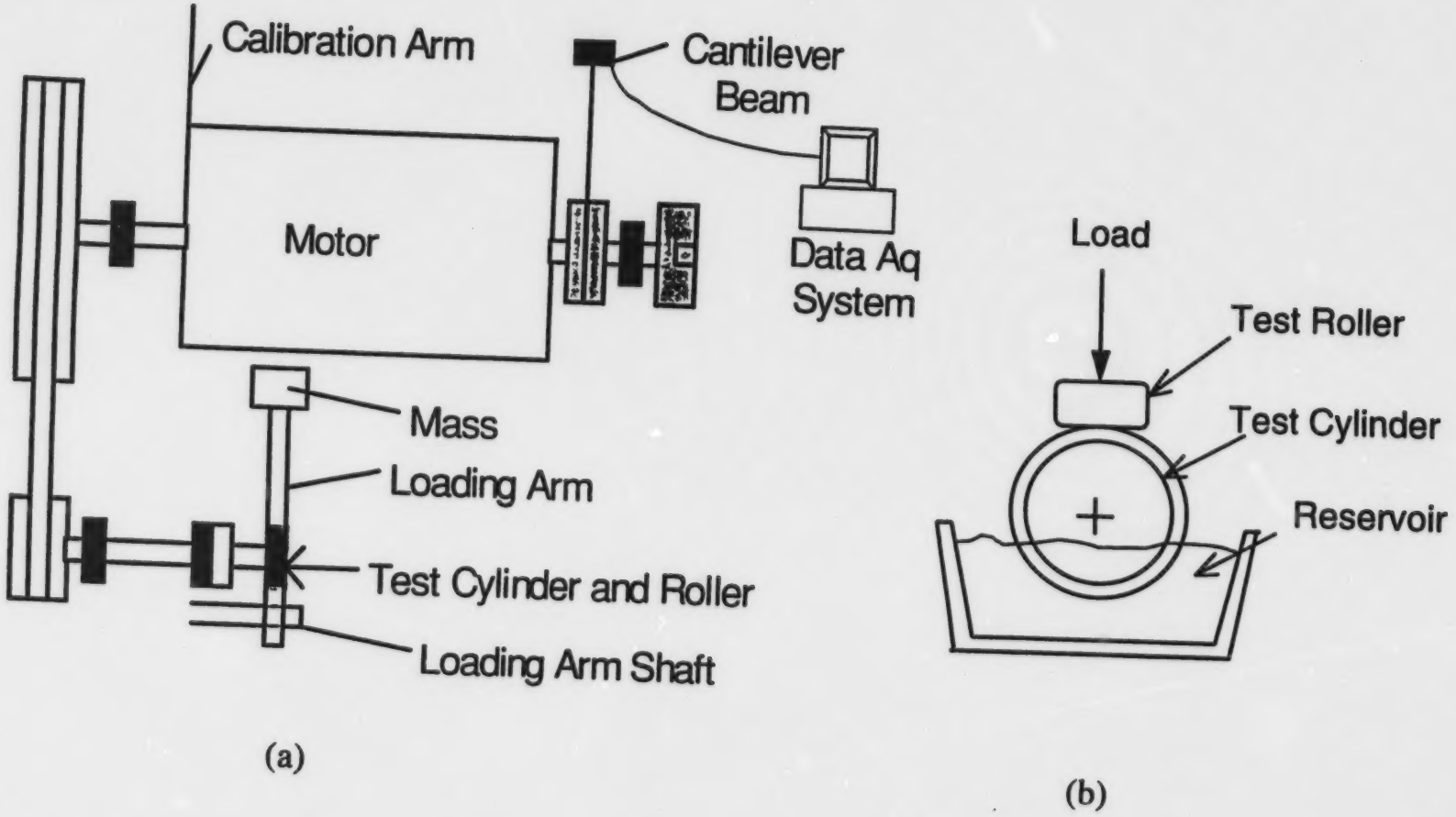

Figure 4. (a): The schematics of the M-ROCLE test apparatus; (b): Actual contact between the test roller and the test cylinders.

Table 11. M-ROCLE test conditions.

Fuel Temperature = 25±1.5°C,
Fuel Capacity = 63 ml,
Ambient Temperature = 24±1.0°C,
Ambient Humidity = 45±5%,
Applied Load = 24.6 N,
Load Application Velocity = 0.25 mm/s,
Hertzian Contact Stress = 896.9 MPa,
Test Duration = 3 min,
Race Rotational Velocity = 600 rpm,
Race Surface Velocity = 1.10 m/s,
Test Specimens:
Falex Test Cylinder: F-S25 Test Rings, SAE 4620 Steel,
Outer Diameter = 35.0 mm, Width = 8.50 mm,
Falex Tapered Test Rollers: F-15500, SAE 4719 Steel,
Outer Diameter = 10.18 mm, 10.74 mm, Length = 14.80 mm.

The M-ROCLE bench test used applies a constant 24.62 N load to a stationary steel bearing roller which rubs against a fuel lubricated rotating steel bearing race or cylinder. The roller and cylinder axes are crossed developing a high theoretical 897 kPa Hertzian stress at the point of contact, similar to the situation in diesel injection pumps. During an individual 3 minute run the computer interfaced steady state motor frictional torque is measured to determine the coefficient of friction developed with the fuel and vegetable ester fluid blends. An environmental chamber is used during testing to control ambient and fuel temperatures and room humidity at 24°C, 25°C, and 45% respectively. Six runs are conducted on each fuel/ester sample. The elliptically shaped wear scars produced on the test rollers during each run are microscopically measured using a computer video system. The ratio of applied load to wear area enables the wear area

stress to be calculated. After determining the unlubricated Hertzian contact stress, a dimensionless Lubricity Number (LN), indicating the lubricating property of the test fuel, was determined using the following equation (8):

$$LN = \frac{\sigma_{ss}}{\sigma_H \times \mu_{ss}}; \qquad \sigma_{ss} = \frac{P}{A}$$

Where:

σ_{ss} = Steady state ROCLE contact stress (Mpa);

σ_H = Hertzian theoretical elastic contact stress (Mpa);

μ_{ss} = Steady state coefficient of friction;

P = Applied load (N);

A = Roller wear scar area (m^2).

The dimensionless LN is indicative of both the wear protection offered and the slipperiness of the fluid. Based on previous work on the M-ROCLE (26), a LN requirement of 1.0 or greater was established as the passing value for a diesel fuel of sufficient lubricity.

Each given test fuel evaluation consisted six, 3 minutes test on the machine followed by a calibration of the reaction torque.

A hydrotreated low sulfur (0.0460 wt%) unadditized No 1 winter diesel fuel designated LSC-43: LSD (DIESEL LIGHT), supplied from Esso Strathcona Refinery in Edmonton, AB, was used as the reference fuel. The density of this fuel was 0.817 g/cm^3

and its kinetic viscosity was 1.27 mm^2/s (cSt) at 40°C. The pour point of this fuel was –51°C while the cetane number was 43.2.

4.3.2. Lubricity evaluation

The 12 samples of biodiesel esters were combined at 1 vol% with the reference diesel fuel to evaluate their efficacy in increasing the lubricating property of the fuel in the M-ROCLE machine. The six replicate data of wear scar areas (WA), coefficients of friction (CF) and Lubricity Numbers (LN), for each of the 12 esters tested at 1 vol% treat rates are tabulated in Tables 12a, b, c, respectively. The average M-ROCLE wear areas, coefficients of friction, and Lubricity Numbers, along with their statistical coefficients of variation (C.V.) based on the six tests, are given in Table 13. The ester/fuel combinations are listed in order of increasing lubricity number. The values of the reference diesel fuel are also included for comparison.

Table 12 (a). Wear area data (in mm^2) from six M-ROCLE replicate evaluation of 1 vol% ester treat rate in No 1 reference diesel fuel.

	1	2	3	4	5	6
No 1 DF	0.3125	0.2956	0.2896	0.3007	0.3068	0.3154
CME	0.2158	0.1918	0.1962	0.2049	0.2051	0.1839
LME	0.2346	0.2225	0.2144	0.2157	0.2205	0.1966
RME	0.1948	0.2028	0.2171	0.2152	0.1713	0.1977
SME	0.2541	0.2581	0.2443	0.2490	0.2223	0.2368
CEE	0.2134	0.2077	0.2112	0.2216	0.2133	0.2340
LEE	0.2005	0.2229	0.1911	0.1957	0.2121	0.1973
REE	0.2428	0.1931	0.2034	0.2394	0.2172	0.2312
SEE	0.2108	0.2134	0.2242	0.2196	0.2216	0.2240
CPE	0.2202	0.2140	0.2312	0.2177	0.2240	0.2047
LPE	0.2373	0.2136	0.2407	0.2217	0.2285	0.2292
CBE	0.2137	0.2025	0.2074	0.2200	0.2201	0.1773
LBE	0.2189	0.1844	0.2119	0.2277	0.2290	0.2189

Table 12 (b). Coefficient of Friction data from six M-ROCLE replicate evaluation of 1 vol% ester treat rate in No 1 reference diesel fuel.

	1	2	3	4	5	6
No 1 DF	0.1094	0.1079	0.1118	0.1139	0.1124	0.1129
CME	0.1064	0.1042	0.1067	0.1062	0.1078	0.1093
LME	0.1054	0.1058	0.1085	0.1082	0.1064	0.1064
RME	0.1014	0.1035	0.1040	0.1064	0.1043	0.1062
SME	0.1069	0.1052	0.1067	0.1089	0.1082	0.1093
CEE	0.1004	0.1009	0.1038	0.1059	0.1069	0.1086
LEE	0.1028	0.1023	0.1049	0.1051	0.1078	0.1064
REE	0.1043	0.1034	0.1035	0.1082	0.1094	0.1080
SEE	0.1014	0.1035	0.1040	0.1063	0.1048	0.1062
CPE	0.0895	0.0897	0.0911	0.0938	0.0954	0.0949
LPE	0.0945	0.0948	0.0953	0.0977	0.0962	0.0974
CBE	0.1034	0.1054	0.1033	0.1042	0.1036	0.1040
LBE	0.1125	0.1131	0.1131	0.1135	0.1127	0.1136

Table 12 (c). Lubricity Number from six M-ROCLE replicate evaluation of 1 vol% ester treat rate in No 1 reference diesel fuel.

Ester	1	2	3	4	5	6
No 1 DF	0.8028	0.8605	0.8478	0.8011	0.7959	0.7708
CME	1.1954	1.3740	1.3118	1.2615	1.2416	1.3653
LME	1.1098	1.1658	1.1805	1.1764	1.1701	1.3128
RME	1.3901	1.3082	1.2162	1.1986	1.2740	1.3069
SME	1.0103	1.0111	1.0529	1.0124	1.1407	1.0608
CEE	1.2806	1.3102	1.2519	1.1695	1.2037	1.0800
LEE	1.3339	1.2032	1.3690	1.3341	1.2008	1.3078
REE	1.0835	1.3746	1.3045	1.0595	1.1557	1.0993
SEE	1.2846	1.2432	1.1776	1.1754	1.1818	1.1535
CPE	1.3934	1.4292	1.3033	1.3447	1.2840	1.4135
LPE	1.2243	1.3556	1.1971	1.2672	1.2485	1.2297
CBE	1.2422	1.2858	1.2817	1.1972	1.2036	1.2421
LBE	1.1146	1.0978	1.1450	1.0619	1.0635	1.1039

Table 13: The average fuel lubricity data and their coefficients of variation for 1 vol% biodiesel esters in No 1 diesel fuel.

Ester/Fuel 1% vol/vol.	Wear Area (mm^2)	Area C.V.* (%)	Friction Coeff.	Friction C.V. (%)	Lubricity Number	LN C.V. (%)
Ref. No 1 Diesel	0.3034	3.29	0.1114	2.04	0.813	4.18
SME	0.2441	5.34	0.1075	1.44	1.048	4.83
LBE	0.2213	3.20	0.1131	0.43	1.098	3.22
REE	0.2212	9.09	0.1061	2.53	1.179	11.01
LME	0.2174	5.73	0.1068	1.19	1.186	5.68
SEE	0.2189	2.57	0.1044	1.77	1.203	4.17
CEE	0.2169	4.41	0.1044	3.17	1.216	6.89
CBE	0.2127	3.65	0.1040	0.83	1.242	3.36
LPE	0.2285	4.35	0.0960	1.40	1.254	4.40
RME	0.2055	4.97	0.1043	1.99	1.284	6.07
LEE	0.2033	5.87	0.1049	2.03	1.291	5.57
CME	0.1996	5.67	0.1068	1.60	1.292	5.51
CPE	0.2186	4.12	0.0924	2.85	1.361	4.41

*C.V.: statistical coefficients of variation.

Table 13 shows that the data were fairly reproducible. For instance, except REE, the coefficients of variation (C.V.) for six measurements of wear scar areas were less than 6.0%. The variations in friction were even smaller; mostly below 3%. Also, ten out of 13 LN measurements had coefficients of variation less than 6.0%, only one test resulted in a C.V. greater than 10% (REE, probably due to the large deviation in WA). The average LN coefficient of variation was 5.42% based on 12 tests without any outliers. In

comparison with the previous version of the ROCLE machine, which had an average C.V. up to 10% based on 12 LN tests when discarding two outliers, the improved M-ROCLE machine achieved higher precision in tribology measurements.

The reference fuel resulted in a large wear scar area of 0.303 mm^2, a high coefficient of friction of 0.111, and an unacceptable Lubricity Number of 0.813.

All 1 vol% biodiesel additized fuel blends had wear scar areas smaller than the reference fuel, as seen from Table 13. SME, sunflower methyl ester, was least effective with a wear area of 0.244 mm^2. The second least effective ester was LPE at 0.288 mm^2. The best-performing ester was CME with wear area of 0.200 mm^2 but was the second highest ranked ester in terms of LN.

The coefficient of friction reveals different results. The two 2-propyl esters, CPE and LPE, provided the lowest friction of 0.092 and 0.096, respectively, among the 12 biodiesels. These products will decrease the fuel consumption when compared to other additives. On the other hand, LBE increased the CF to 0.113, which was above that of the reference fuel at 0.111. The remaining esters had similar friction values.

The Lubricity Number is based on the ratio of wear area and the coefficient of friction. All of the 1 vol% biodiesel additives improved the LN of the reference fuel to above the passing value of LN>1 on the M-ROCLE, as shown in Figure 5, where the esters were plotted in ascending order of Lubricity Number. CPE led the field of 12 esters with LN = 1.36 at 1 vol%, which was mainly due to its very small friction coefficient of 0.092, the smallest among all the 12 samples. CME and LEE are the second best additives, with LN = 1.29. The boost in lubricity for the CME and CPE at the 1 vol% treat rate was 59% and 67%, respectively.

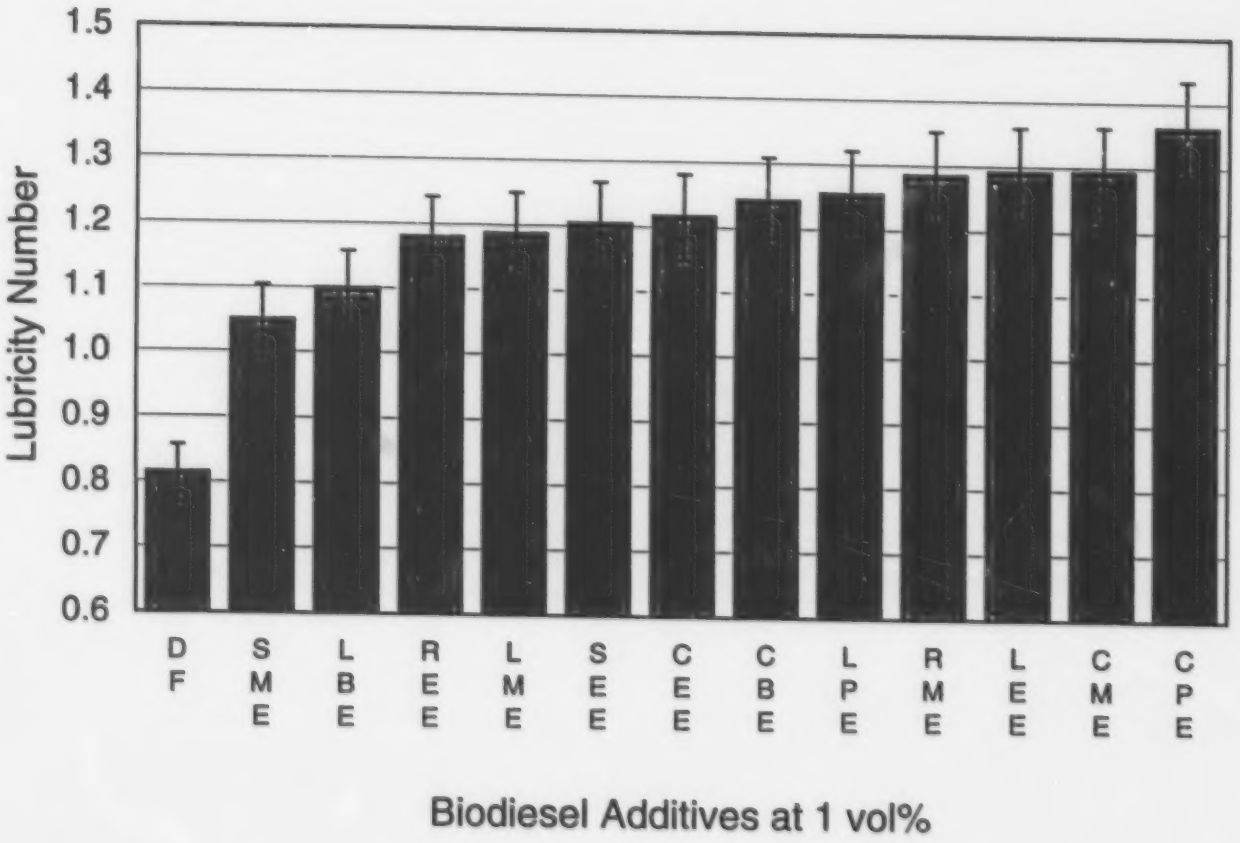

Figure 5. M-ROCLE Lubricity Number results for 1vol% biodiesel additives.

Because of their superior lubricity performances, two of the esters, canola methyl and 2-propyl esters (CME and CPE) were tested for fuel lubricities at different treat rates in the reference fuel. Also, tested on the M-ROCLE were the neat esters (100% treat rate) and the plain reference fuel (0% treat rate). The test results for the various blend ratios of CME and CPE to those of the reference fuel are given in Tables 14 and 15, respectively. Figure 6 shows a near semi-log linear relationship between LN and the ester treat rates. The LN of 0.811 of the reference diesel was plotted as the "zeros" treat rate in Figure 6. It may be noted that the logarithm relationship below 0.1vol% may not exist since there is no zero point on a log scale for the reference fuel. It is found that blending as little as 0.1 vol% CME to the reference fuel boosted the fuel LN to 1.046 and exceeded the passing value of LN = 1.0 in the M-ROCLE test. Further increasing the CME treat rates to 0.25, 0.5 and 1 vol% provided an improvement over the LN of the reference fuel by 45, 51 and 59%, respectively. Similarly, the boost in lubricity for the CPE at the 0.25 and 1 vol% treat rates was 50 and 67%, respectively. The rates of increases in LN values became lower as the ester concentrations exceeded 1 vol% in the reference fuel.

Table 14. M-ROCLE lubricity survey results of different CME concentrations in No 1 diesel fuel.

Fuel Sample	Wear Area (mm^2)	Area C.V. %	Friction Coeff.	Friction C.V. %	Lubricity Number	LN C.V. %
Ref. No 1 Diesel	0.3034	3.29	0.1114	2.04	0.813	4.18
0.10 vol% CME	0.2509	3.20	0.1046	1.05	1.047	2.27
0.25 vol% CME	0.2290	6.62	0.1022	1.08	1.177	7.16
0.50 vol% CME	0.2220	2.35	0.1008	1.55	1.228	3.37
1.00 vol% CME	0.1996	5.67	0.1068	1.60	1.292	5.51
100vol% CME	0.2030	3.01	0.0859	1.91	1.577	4.91

Table 15. M-ROCLE lubricity survey results of different CPE concentration in No 1 diesel fuel.

Fuel Sample	Wear Area (mm^2)	Area C.V. %	Friction Coeff.	Friction C.V. %	Lubricity Number	LN C.V. %
Ref. No 1 Diesel	0.3034	3.29	0.1114	2.04	0.813	4.18
0.25 vol% CPE	0.2172	1.64	0.1038	0.91	1.218	1.62
1.00 vol% CPE	0.2186	4.12	0.0924	2.85	1.361	4.41
100 vol% CPE	0.1870	3.34	0.0916	1.94	1.604	2.46

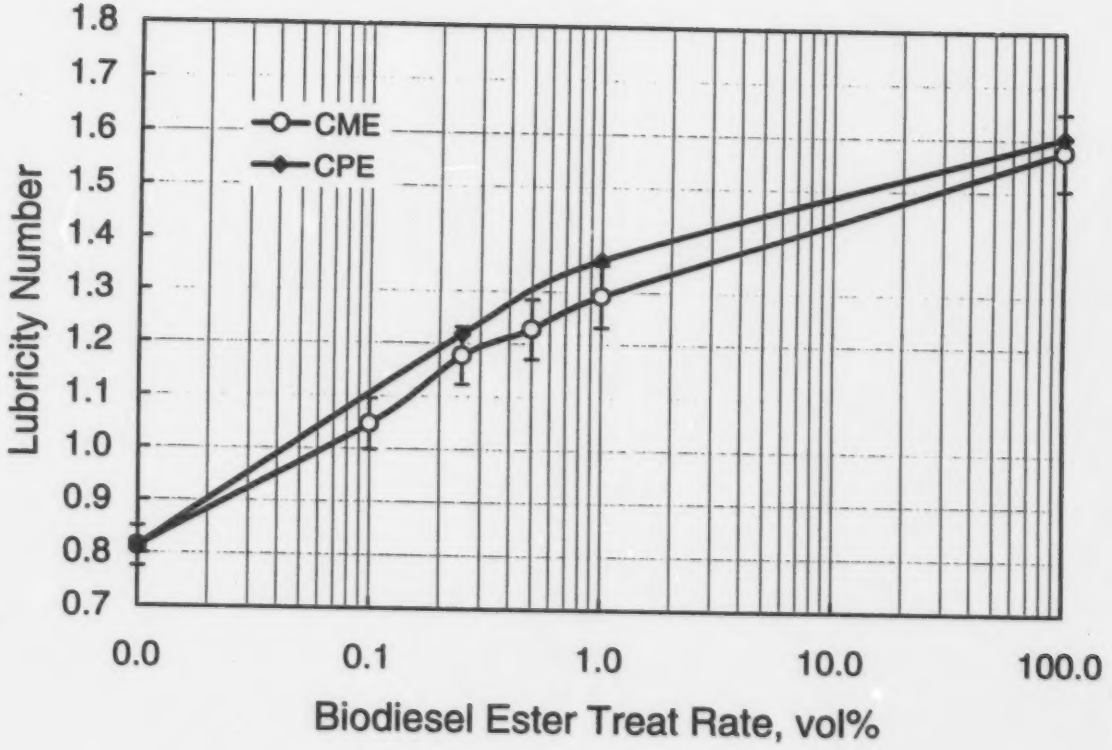

Figure 6. Effects of CPE and CME treat rates on Lubricity Number.

4.3.3. Statistical Analyses

To assess whether and how the different vegetable oils and alcohols used for the ester preparation affect the lubricity during the M-ROCLE tests, the data at 1 vol% treat rate were statistically analyzed as a completely randomized factorial experiment, which involved two independent factors (or treatments): vegetable oil (fatty acid) source and alcohol type. The oil source factor is equivalent to the effects of fatty acids in the esters. A statistics software, SuperANOVA (39) was used in the computation.

The results of the statistical analysis are summarized in Table 16 as the ANOVA (ANalysis Of VAriance) tables for the wear area, coefficients of friction and Lubricity Number as the dependent variables. The sum of square (SS) was computed for each of the effects (main, interaction and error). Each sum of square divided by its degrees of freedom (df) gives a mean square (MS). The mean square due to treatment (MST), measures the variation between the treatment levels, whereas the mean square due to error (MSE) measures the variation within all observations (random error). If the null hypotheses of no treatment effects are true, then all MST, MSI (MS due to interaction) and MSE estimate the variance of the random experimental error. Otherwise, the MST or MSI will be larger than MSE. The appropriate statistic for testing the equality of the treatment effects is given by

$$F = MST \text{ (or } MSI)/MSE.$$

The ratio F has an F distribution with (v1, v2) degrees of freedom, where v1 is the df associated with MST (or MSI) and v2 is the df associated with MSE. The probability of obtaining an F value with the same degrees of freedom as the computed one if the null

hypothesis is true is quantified by the p-value (40). Therefore, a large F value and a small p-value imply that the data do not support the null hypothesis.

Table 16. Analysis of Variance for the M-ROCLE lubricity evaluation.

Dependent variable: Wear Area:

Source of Variation	Degree of Freedom (df)	Sum of Squares (SS)	Mean Square (MS)	F	p-value
Fatty Acid	3	4.412E-3	1.471E-3	11.957	.0001
Alcohol	3	1.763E-3	5.876E-4	4.777	.0047
Interaction	5	4.239E-3	8.478E-4	6.893	.0001
Error	60	7.380E-3	1.230E-4		

Dependent variable: Coefficient of Friction:

Source	df	SS	MS	F	p-value
Fatty Acid	3	1.334E-4	4.448E-5	11.645	.0001
Alcohol	3	1.485E-3	4.949E-4	129.555	.0001
Interaction	5	2.015E-4	4.029E-5	10.549	.0001
Error	60	2.292E-4	3.820E-6		

Dependent variable: Lubricity Number:

Source	df	SS	MS	F	p-value
Fatty Acid	3	.183	6.083E-2	12.672	.0001
Alcohol	3	.119	3.968E-2	8.266	.0001
Interaction	5	.189	3.781E-2	7.877	.0001
Error	60	.288	4.801E-3		

In the ANOVA table for the wear area, the largest calculated F-value was 11.96 for the effects of oil (fatty acid). This suggests that the differences in oil source of the biodiesel esters, i.e., differences in their fatty acid components, have a strong effect on the wear area (when the biodiesel ester were blended at 1 vol% treat with the fuel and tested in the M-ROCLE machine). In the ANOVA table for the coefficients of friction, the p-values were 0.0001 for the two main effects as well as the interaction effects. Moreover, a very large F-value of 129.6 was computed for the alcohol factor. Thus, the types of oil and alcohol used to prepare a biodiesel also affect its ability (at 1% treat rate) of reducing friction. In the ANOVA table on the Lubricity Number, all three p-values were small, implying that the esters made from different oil (fatty acids) or from different alcohol (alkyl tail group) have large effects on lubricity improvement.

The mean values of wear area when using the canola, linseed, rapeseed and sunflower esters at 1 vol% treat rate during the M-ROCLE test are presented in Table 17. In the Table, each mean value was averaged from all the replicates of the different alkyl esters made from the same oil. It can be seen that the sunflower esters on average produced larger wear scar areas (0.232 mm^2) compared to the esters made from the other three oils. The sunflower methyl ester was the least effective lubricity additive among the 12 esters, with an average wear area of 0.244 mm^2 (Table 13). The question was raised as to if any particular fatty acid in the sunflower oil was more responsible for the observed higher wear. The predominant fatty acid in the sunflower oil esters is linoleic acid (18:2) averaging at 68% (Table 2). When the mean wear areas from Table 17 were plotted as a function of the linoleic acid concentrations (in the fuel), a descending line was obtained. It seems to suggest that the lower the linoleic acid concentration, the less

was the wear area. However, such a conclusion does not agree with the data while using different ester treat rates. These generally show the higher the treat rate, the higher the linoleic acid concentration, and the better the lubricity of the fuel. Plotting other compounds also could not identify one single fatty acid, which is responsible for the wear area reduction or lubricity improvement (41).

Table 17. Mean wear area for 1 vol% biodiesel (in reference fuel) derived from various vegetable oils.

Oil source	Count	Mean WA	Std. Dev.	Std. Error
Canola	24	0.212	0.012	0.002
Linseed	24	0.218	0.014	0.003
Rapeseed	12	0.213	0.017	0.005
Sunflower	12	0.232	0.016	0.005

In Figure 7, the mean wear area was plotted against the non-linoleic acid in the fuel. In addition to the data at 1% treat rate, the mean wear area data obtained at different treat rates (0.1 to 100%) with canola esters were also included. The non-linoleic acid in the fuel was calculated as (100 – linoleic acid concentration of an ester) times the treat rate. A near semi-log descending linear relationship between WA and the non-linoleic acid was obtained. This figure implies that certain non-glyceride substance(s) even in trace amounts in the esters, which are yet unknown to us, may play an important role in improving lubricity in the biodiesel esters.

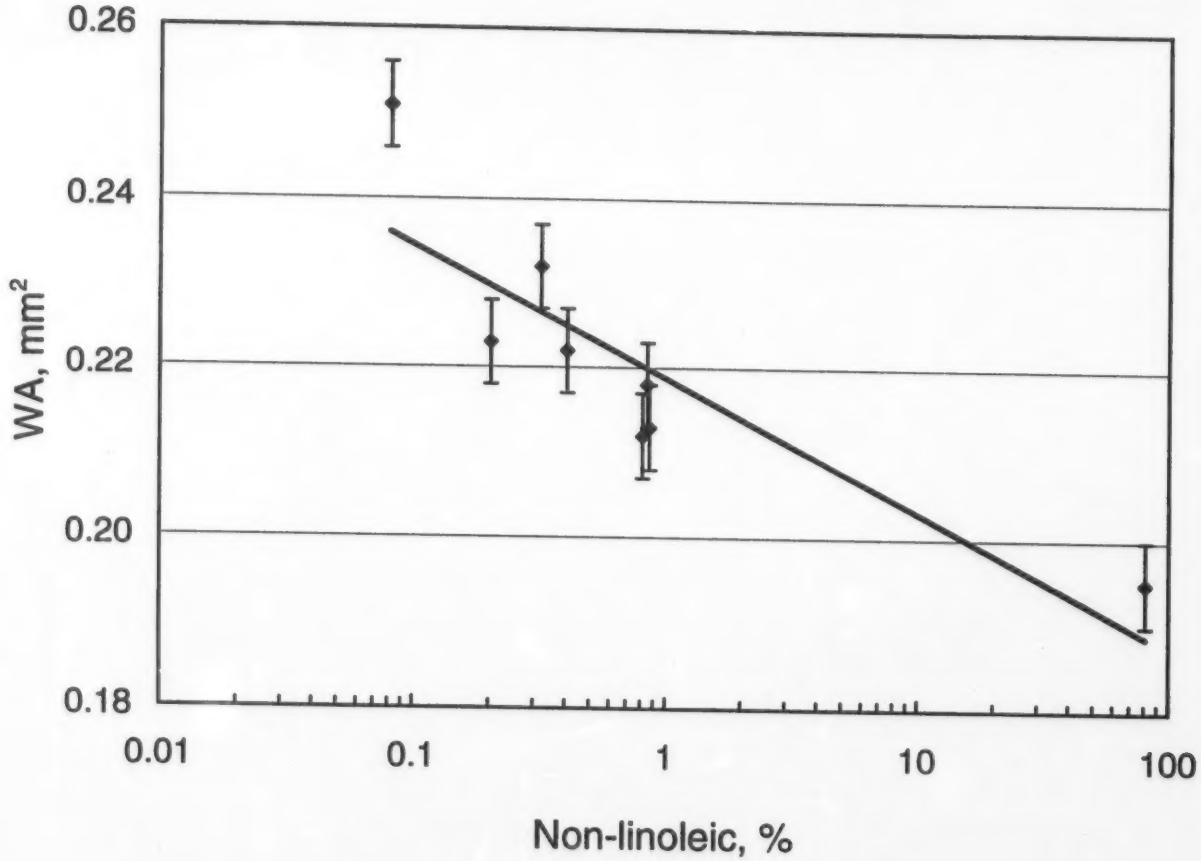

Figure 7. Non-linoleic acid concentration on the wear area.

Polar hetero-cyclic compounds containing N and/or O atoms have recently been viewed as potent lubricity agents naturally present in diesel fuels. However, they may not be responsible for the biodiesel lubricity enhancement, since these compounds are not found in vegetable oil derived biodiesel esters. More study and understanding is required on the theoretical mechanism of biodiesel lubricity.

4.3.4. Selection of a lubricity additive

During the lubricity evaluation on the M-ROCLE machine, two canola oil based esters, CPE and CME, have demonstrated to be the best additives in terms of LN. As stated earlier, the LN of the ester-additized fuel was 1.36 for CPE and 1.28 for CME at 1 vol% treat rate, with the CPE additized fuel performing somewhat "5% better" than the CME additized fuel. However, there are two major factors that disfavor the development of CPE as a commercial diesel fuel lubricity additive. The first factor is the cost of alcohol associated with the ester production. For example, the local bulk price for the technical grade anhydrous methanol was quoted as 0.63 $/kg; while that for anhydrous 2-propanol was 1.61 $/kg (Van Waters & Rogers Ltd., Saskatoon), or nearly 2.5 times more expensive. This difference alone will translate into a 10 c/L more in the production of CPE than that of CME. The second factor is the complexity that would be involved with the CPE production. As CME can be catalyzed at ambient temperature using common alkali catalysts such as KOH or NaOH, transesterification to CPE generally requires higher reaction temperatures and sodium methoxide or even metal sodium as catalysts. Dealing with such hazardous chemicals needs special vessels and equipment, thus could further increase the capital costs of the production. In addition, catalyst costs of using

methoxide or metal sodium could be ten fold more than the KOH. When all is added up, the significantly higher production costs associated with CPE than CME probably will offset the mere 5% difference in the lubricity performance between the two esters. Since the objective of this project is to develop an economical and efficient process of producing lubricity additives, the group selected CME, canola methyl ester, as the best candidate for a biodiesel ester lubricity additive, based on both the lubricity enhancement and the economical considerations. Accordingly, the following studies on process development and cost analyses will focus to the production of canola methyl ester.

4.4. Canola Methyl Ester Production and Economics

In this section, a continuous flow process for producing canola methyl ester is proposed, and the costs associated with the production as well as the potential investment returns are assessed.

4.4.1. Process development

The development of the proposed process follows the design philosophy of using technologies that are simple and "cleaner". Even as the canola methyl ester is marketed as a high-performance fuel lubricity additive, it needs to be competitive in price with other similar products currently available on the additive market. Using simple, standard chemical engineering unit operation in the production allows the process to be cost effective and thus minimize the production cost of the ester. On the other hand, a "cleaner" process means to minimize the waste generated from the production and thereby reduces the pollution and protects the environment, which eventually will also lead to lower costs. A "cleaner" process will be achieved through combined effects of maximizing the yield, recycling unreacted reactant and minimizing process water.

The concept for the process of canola methyl ester production is illustrated in a block diagram (Figure 8), which involves four sectors:

(1) Catalyst preparation, in which the solid catalyst is mixed and dissolved in methanol prior to the reaction.

(2) Reaction and liquid - liquid separation, in which vegetable oils obtained from the crusher react with the catalyst containing alcohol in a two-step reaction

scheme, and each step is followed by a phase separation of crude ester from crude glycerol.

(3) Ester purification, in which the excessive alcohol necessary for the reaction is recovered and impurities in the crude ester are removed.

(4) Glycerol purification, in which crude glycerol is recovered.

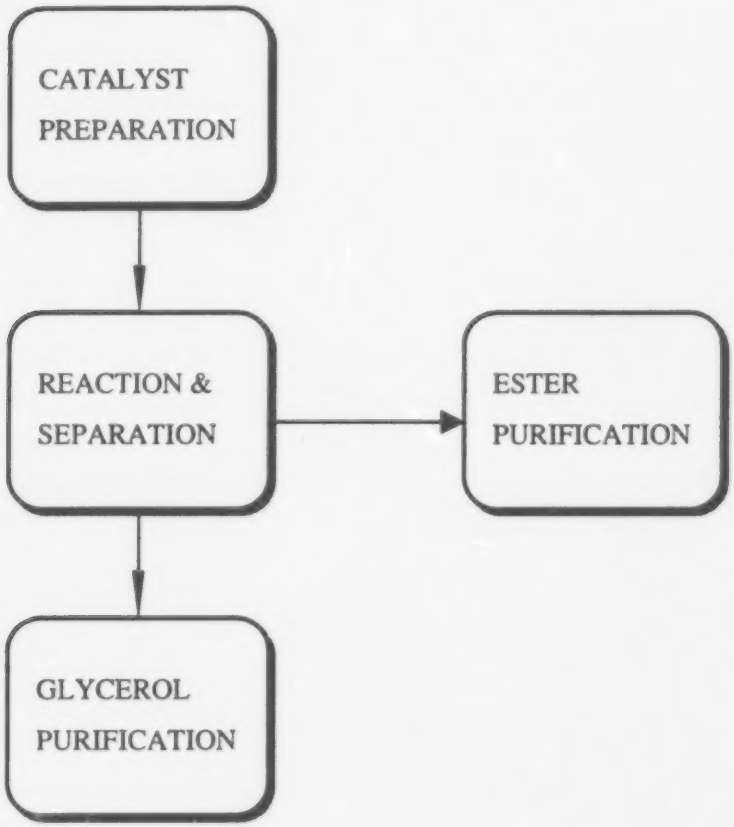

Figure 8. Block diagram of canola methyl ester production.

4.4.2. Process flowsheet

A flowsheet of a continuous flow process for the canola methyl ester production is shown in Figure 9. The major material streams and major pieces of equipment are drawn on the figure, auxiliary equipment such as pumps as well as feed and products storage tanks are omitted for simplicity. In addition, the pretreatment steps of oil and methanol are excluded since the technology is well known. For example, the flowsheet starts with refined oil; in a plant, the oil is crushed from canola seeds (these can be either premium grade or heat damaged) then refined using the conventional technologies available from any prairie crushers. A description of the flowsheet is given below by following the four sectors shown in the block diagram Figure 8.

Catalyst Preparation

First, methanol is continuously sent by a metering pump from an alcohol storage tank (*02*) to a catalyst mixing tank (*03*). Potassium hydroxide pellets are introduced as the solid catalyst at a predetermined rate through a chute and a screw conveyor (*01*) to the mixing tank, and are dissolved in methanol under continuous stirring. The stirred tank is equipped with a cooling coil or a cooling jacket in order to remove the excessive heat released from dissolution of the solid catalyst. The temperature of the catalyst-methanol solution should be controlled under 64 °C, the boiling point of methanol, to prevent it from evaporating.

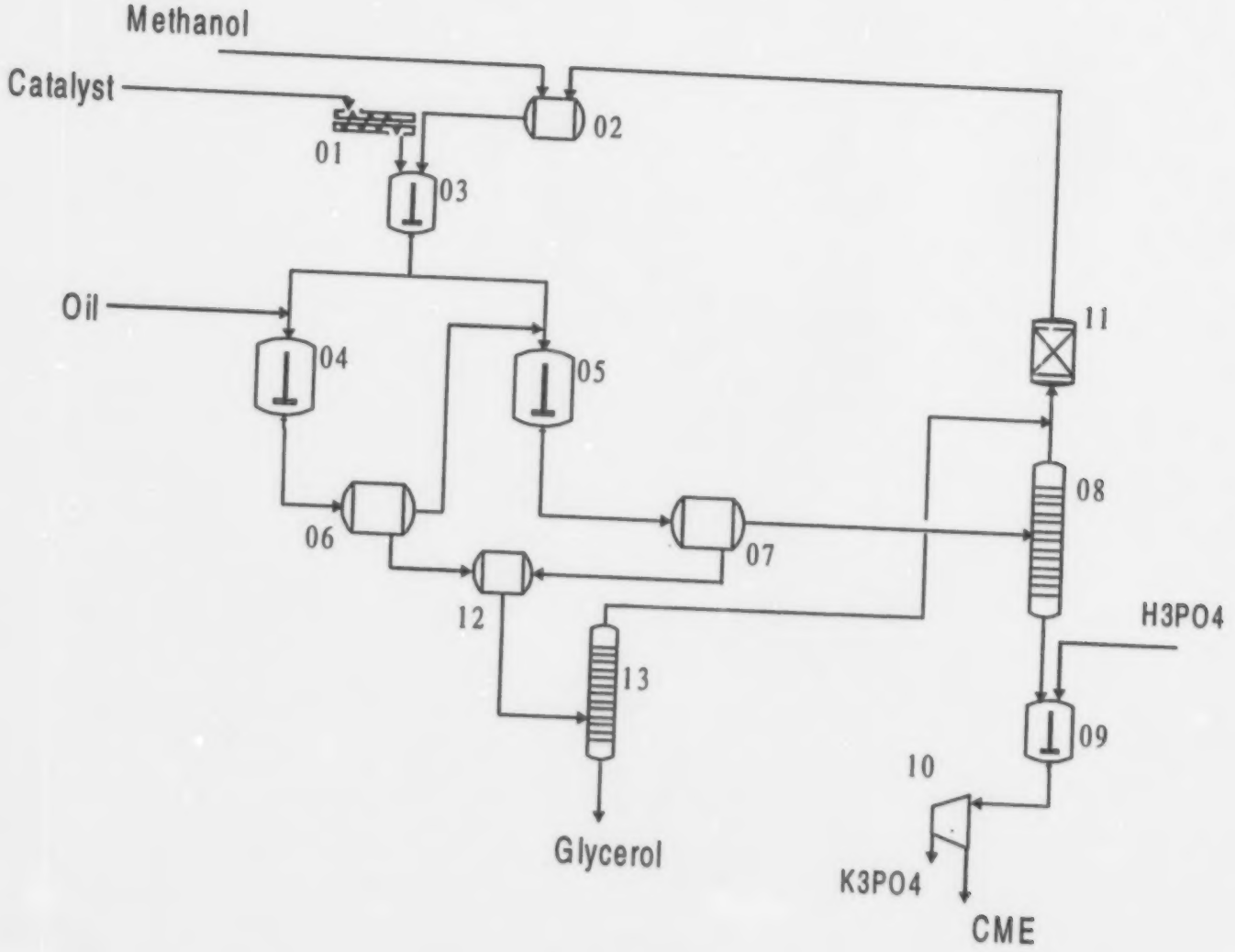

Figure 9. Flowsheet of a canola methyl ester production plant.

Reaction and ester - glycerol separation

The reaction of canola oil transesterification with methanol is carried out in two steps, both at ambient temperature and pressure. In the first step, purified canola oil is continually fed by metering pump to the first stirred reactor (*04*), and mixed together with the catalyst-containing methanol from tank (*03*) at a predetermined ratio. The reaction contents are vigorously stirred in the reactor and the residence (reaction) time is maintained at approximately 20 min. The product stream leaving the reactor (*04*) is sent to a plate separator (*06*) where the reaction contents are separated by gravity into two phases, a light liquid phase, consisting of canola methyl ester as well as unreacted vegetable oil, and a heavy liquid phase of crude glycerol. After the separation, the light phase is sent to the second stirred reactor (*05*), and mixed with additional catalyst-containing methanol from tank (*03*) to achieve nearly complete conversion of the oil. The reaction products are then sent to the second plate separator (*07*) for further separation of the light crude ester from the heavy crude glycerol. The lighter crude methyl ester from the separator (*07*) is directly forwarded to its purification section, while the crude glycerol from the two separators is combined in a storage tank (*12*) before sending for glycerol post treatment section.

CME purification

The crude canola methyl ester leaving the second plate separator (*07*) contains impurities like methanol, soap and spent catalysts. For purification, the crude ester is first send to a distillation column (*08*), where the excessive methanol, which is used as a feed for the reaction, is removed from the crude ester by ambient pressure distillation.

From the top of the distillation column, methanol is recovered and then passed through a dryer (*11*) packed with conventional drying agent to remove any possible moisture. The anhydrous alcohol leaving the dryer is then returned to the methanol storage tank (*02*) and combined with fresh methanol feed before entering into the reaction loop again. Meanwhile, the methanol-free esters, which are obtained from the bottom of the distillation column (*08*), are charged into a neutralizing tank (*09*). A small stream of phosphoric acid (85% H_3PO_4) is also added to the tank at a ratio of 1-2 vol% based on the ester analysis, and the acid reacts with the residual alkali catalysts in the ester to form potassium phosphate salt. The effluent of the neutralizing tank (*09*) is sent to a liquid-liquid centrifugal separator (*10*) so that the salt and soap are separated from the ester. The lighter liquid flowing out the centrifugal separator is the purified final product, canola methyl ester, and is filtered and stored in storage tanks (not shown). The heavier phase from the centrifugal separator is a byproduct, a mixture of potassium phosphate salt and soap, which can be used as fertilizer.

Glycerol treatment

The crude glycerol phase from the plate separators also contains some methanol and residual catalyst. The methanol is removed and recovered in a distillation column (*13*) and then sent for recycling together with the methanol recovered from the distillation column (*08*). The methanol-free glycerol obtained from the bottom of the column (*13*) is a byproduct of the process. It can be sold to pharmaceutical industry or be used in the site as an intermediate for further synthesis of fine chemicals.

In summary, following design features can be identified from the proposed process:

(1) A two-step reaction: This can maximize the transesterification yield to the methyl ester within a short reacting period.

(2) Recycling of methanol: By recovering excessive methanol and recycling it for further reaction, the alcohol feed usage can be minimized, and air pollution reduced.

(3) Use of a very small amount of water for washing (ester purification): This can improve the ester quality while minimizing water pollution.

4.4.3. Approach for cost analysis

The analysis followed is based on the continuous-flow transesterification process proposed in the preceding section. The methodology used in the production costs analyses is based on the ANL Biomass Cost Estimation Guide (42), as illustrated in a case study of beef tallow conversion to its methyl ester by Nelson and Schrock (43). The production cost was determined by estimating the capital and operating cost, and credits were included for process byproducts, glycerol and canola meal. The plant capacities were based on annual production of 1 million liters of canola methyl ester, which is approximately 19 barrels per day, using canola oilseed as the feedstock and operating continuously 330 days per year.

4.4.4. Capital costs

The total capital costs for the plant were determined using the factor method proposed by Guthrie (44). An overall capital costs factor, based on per liter of ester, included the direct costs for all the equipment in the entire plant as well as the indirect

costs such as engineering cost and construction overhead. The annual ester productions were then multiplied by this costs factor to give the fixed total capital costs or fixed capital investment for the plant.

The capital coast factor applied to this analysis was derived from two recent economic studies found in the literature on biodiesel production with compatible plant capacities as the one we have proposed. In one study on rapeseed methyl ester production, Gavett et al. (45) applied a factor of US$ 0.72 per gallon of ester for an operation of a 3 tons of oil seed per day. In the second study, Nelson and Schrock (43) used a factor of US$ 1.0 per gallon of ester for a 3 million gallons of tallow methyl ester per year unit. These factors in US dollars per gallon were converted into Canadian dollars per liter using the ratios of 1.0 Can$ = 0.69 US$, and 1.0 gallon = 3.785 liters. The changes due to inflation in the overall plant costs over the years from 1993 to 2000 were taken into consideration by using the Chemical Engineering Plant Cost Index (46), with CE Annual Index for 1993 = 359 and Annual Index for 2000 = 393, respectively. As a result, the two costs factors cited above can be converted to Can$ 0.30 and 0.42 per liter of ester, respectively, for year 2000. A less than average value of 0.35 $/liter was selected as the capital coast factor for this analysis, as the capital costs for a canola methyl ester plant would be comparable to that of a rapeseed methyl ester one but would be less than that of a tallow ester plant.

The costs of land and contingencies were not included in the cost estimate.

4.4.5. Operating costs

Operating costs include the costs for feedstock and supplies, labor and fringe expenses, overhead, utilities, repair and maintenance, and insurance.

The total cost of a feedstock is calculated based on its unit price and the annual demand. The feedstock demand is estimated by the annual plant production and the process yield (refer to section 4.4.6.). The unit price of canola oilseed varies from year to year, an average value of 300 Can$/ton was found from the Winnipeg future market listing, and was used in this analysis. The unit cost for methanol was quoted from a local distributor (Van Waters & Rogers Ltd., Saskatoon) at 0.60 Can$/kg (0.47 $/liter). This value seems high in comparison with that of 0.55 US$/gallon quoted by Nelson and Schrock (43), which could be converted to 0.21 Can$/liter (at year 2000). The prices for the catalyst and other chemicals were obtained from catalogs.

The fixed operating costs of maintenance materials, insurance, as well as that of utilities were based on percentages of the total capital cost. The percentages and basis for the variable operating costs (feedstock and supplies) are listed in Table 18.

4.4.6. Yield and feedstock

The raw material demands were based on an overall 98 wt% yield from canola oil to canola methyl ester (CME). From the reaction stoichiometry and a catalyst usage of 1 wt% based on oil, for each ton of oil, 0.1 tons of methanol and 0.01 tons of KOH as the catalyst were required as the input. The output would be approximately 0.98 tons of CME (or 1,126 liters), 0.098 tons of glycerol, 0.01 tons of spent catalyst and 0.022 tons of unreacted oils. Canola oil was often extracted at a press efficiency of 42% from oilseeds, which converts to 2.4 tons of seed producing one ton of oil. Consequently, for producing one million liters of CME annually, the plant requires approximately 2,131 tons of oilseeds (to give 888 tons of oil), 89 tons of methanol and 8.9 tons of KOH.

4.4.7. Credits

At least two types of process byproducts from the proposed ester production plant were available for credit: canola oilseed meal and glycerol.

From every 100 kg of canola oilseeds, approximately 42 kg of canola oil can be extracted (at a press efficiency of 42%); the remaining 58 kg becomes the canola meal. Since the meal from the biodiesel plant is not vigorously extracted (no solvent extraction in order to lower the costs), it contains some fat and also in average contains 39 wt% of protein. Such a meal is suitable for use as an animal feed, and can be sold on the average at Can$ 160 per ton (47).

The amount of glycerol resulting from the transesterification reaction is approximately 10 wt% of the ester produced. Therefore, from the proposed plant of 1 million liters ester, 87 tons of glycerol will be generated each year. The glycerol can be used to produce surfactants, pharmaceuticals and other value-added products, and can be sold for between 0.87 to 1.38 Can$/kg depending on the purity (1, 43, 45). An average unit price of 1.05 Can$/kg was selected for glycerol credit in this analysis.

4.4.8. Basis of assessment

Table 18 summarizes the assumption and costs of the various parameters used to determine the production cost of canola methyl ester. All cost analysis was based on Canadian dollars, and it was expected that a pilot-scale plant will be built in the vicinity of Saskatoon in the near future.

Table 18. Parameters used in the total cost analysis.

Plant Capacity (annual)	1,000,000 L of canola methyl ester
Time (year)	2001
Place	South Saskatchewan
Currency	Canadian Dollars
Annual Operation days	330 Days
Maintenance (labor and material)	2 % of Total Capital Costs
Insurance	1 % of Total Capital Costs
Utilities	10 % of Total Capital Costs
Feedstock Price	
Canola oilseeds	300 $/ton
Anhydrous methanol, tech grade	0.6 $/kg
Catalyst Price	1.5 $/kg
Byproduct Price	
Canola meal	160 $/ton
Glycerol	1.05 $/kg
Interest Rate	10 %
Plant Life	15 years

4.4.9. Total cost analysis

The total production cost analysis for the continuous flow, 1 million liters per year canola methyl ester unit was conducted, and the results are shown in Table 19. The total capital cost of the plant will be $350,000 based on a capital cost factor of 0.35 $/liter of ester. The real annual cost of capital was subsequently calculated by assuming a 0.217 fixed charge rate for 15 year book life and no tax preferences, as delegated from the ANL Biomass Cost Estimation Guide (42). The annual costs for individual feedstock were calculated from the total feed demand (section 4.4.6.) and respective unit prices listed in Table 18. By including other operating costs, many of which were tied to the fixed percentage of the total capital cost, the total annual operating costs was estimated as $831,850, while the total annual cost was $1,008,980. After the credits received from the sale of byproducts were subtracted, the total net annual cost for the plant became $718,590. This translates into a cost of approximately 0.72 $/liter for making canola methyl ester.

Table 19. Total cost analysis associated with canola methyl ester production (Continuous flow process, 1 million liters per year).

	TOTAL COST ANALYSIS	
I	Total Capital Costs	$350,000
II	Real Annual Cost of Capital [0.217 of I]	$75,950
III	Total Annual Operating Cost	$831,850
IV	Sales and Administration [10% of (II+III)]	$90,780
V	Working Capital [1/12 of (II+III+IV)]	$83,215
VI	Annualized Cost of Working Capital [12.5% of V]	$10,400
VII	Total Annual Cost [II+III+IV+VI]	$1,008,980
VIII	Byproduct Credit	$290,390
IX	Total Net Annual Cost [VII-VIII]	$718,590
X	Total Production Cost per Liter	**$0.72**
III	Operating Cost	
	Materials and Supplies	
	2,132 tons of canola oilseeds	$639,600
	89 tons of anhydrous methanol	$53,400
	8.9 tons of KOH	$13,350
	Other chemicals	$5,000
	Direct Labor	$50,000
	Overhead and Fringe Benefits [50% of direct labor]	$25,000
	Utilities	$35,000
	Maintenance	$7,000
	Insurance	$3,500
	Total Annual Operating Costs	$831,850
VIII	Byproduct Credit	
	87 tons of glycerol	$91,350
	1,244 tons of canola meal	$199,040

4.4.10. Sensitivity analysis

Parameter sensitivity analyses were performed to determine the effects of varying feedstock prices, byproduct credits, and the utility costs, on the CME production cost. The unit values listed in Table 18 were taken as the base case. Each parameter was then individually changed ±10 and 20% off the base value, while all others were kept constant, to recalculate the production cost of CME. The results are presented in Table 20 and Figure 10.

Table 20. Sensitivity analysis of various parameters on CME production cost ($/L).

Factors	−20%	−10%	Base	+10%	+20%	Difference on CME by each 10% change
Oilseed	0.58	0.65	0.72	0.79	0.86	+7 c/L
Methanol	0.71	0.71	0.72	0.73	0.73	+0.6 c/L
Meal	0.76	0.74	0.72	0.70	0.68	−2 c/L
Glycerol	0.74	0.73	0.72	0.71	0.70	−1 c/L
Utility	0.71	0.72	0.72	0.72	0.73	0.4 c/L

Canola oilseed cost had the greatest impact on the production cost, as shown in Figure 10. The CME production cost rose nearly 7 c/L when the seed price increased by 10%, from 300 to 330 $/ton. Any further 10% variation on seed prices will cost additional 7 c/L on CME production, as indicated by the value shown in the last column of Table 20.

A difference of slightly less than 0.6 c/L occurred when the methanol price change 10% from the base value of 0.6 $/kg.

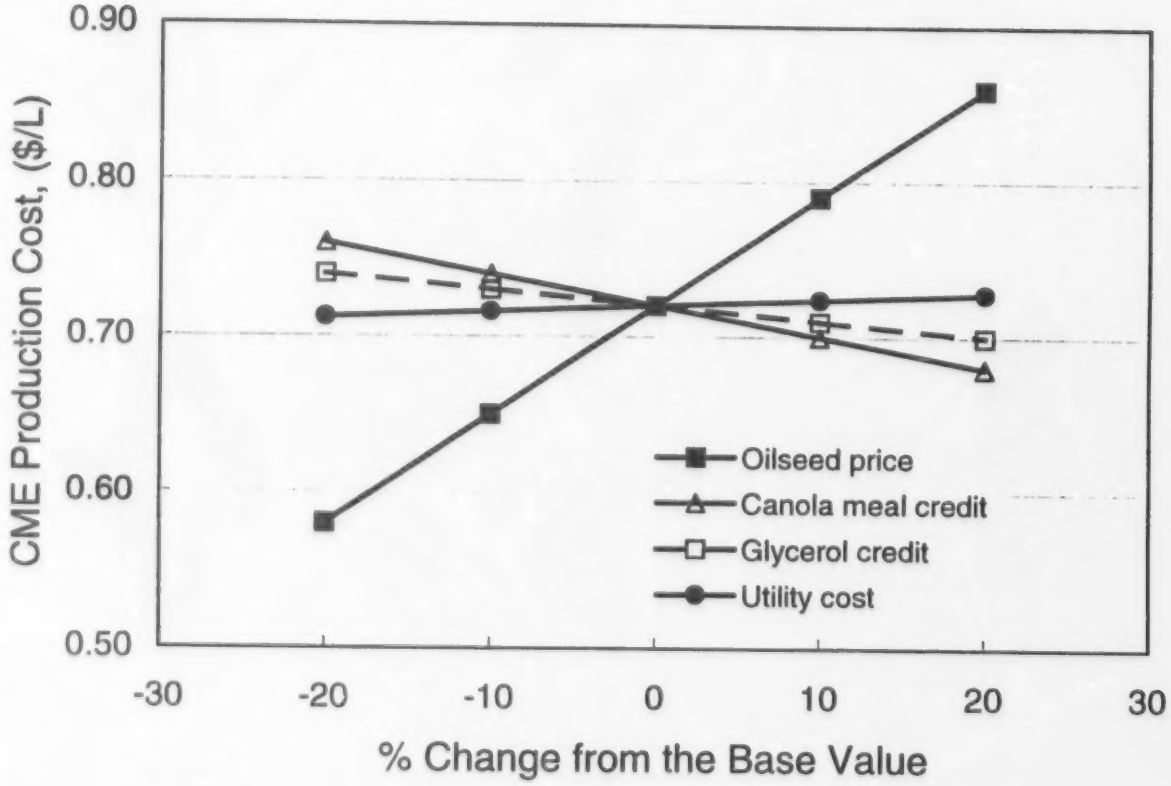

Figure 10. Sentivity analysis of various parameters on CME production cost.

The canola meal credit also showed large effects. It will lower the production cost of CME by an approximately 2 c/L if the meal price increases by 10%. Currently, new technologies are being developed in the Province, which are aimed at improving the meal's nutritional quality. If they are successful, the meal will be worth more, and thus could bring down the cost of methyl ester production substantially.

A small deviation in utility costs from the base value would have insignificant effects on CME production cost. The utility costs in this analysis were projected at 10% of the total capital costs, or $35,000. If this rate was increased to 15%, or if $52,500 was allocated for the annual utility costs due to higher energy consumption of the facility, the production cost of CME would rise 2 c/L to 0.74 $/L.

4.4.11. Economic return

In this last part of the economic analysis, we estimated the return on canola methyl ester investment, in terms of discounted cash flow and the maximum return rate. The return of investment is the expected payoffs to investors, which can be bank, governmental agency, company or individual entrepreneurs, who loan money to build up the CME production plant. The rate of the return is dependent on the size of the after tax profit of the plant, which in turn is a function of the plant revenue (sales), the plant operating costs, and the tax rate.

The plant revenue comes from the sales of CME as well as the by-products, glycerol and meal. The annual by-product credits have been calculated to be $290,390, as shown in Table 19. To determine the revenue from CME, we need to have a selling price of CME. CME as a lubricity additive can be sold either by retail or by bulk. Presently, the retail prices for various substitute lubricity products range from $8.95 to

$35.00 per liter (48). High pricing for many of these products is due to that they are multi-attribute additives in addition to lubricity. It is envisioned that a better way to distribute the CME as a lubricity additive is to sell it bulk, to fuel refineries or blenders before the fuel is sent to the pumping stations. By selling CME in bulk, a profit of $1.00 per liter should be a reasonable estimation. Therefore, a selling price of $1.72 per liter for CME was used. For the 1 million liters plant, the annual revenue from sales of CME would be 1.72 million dollars; and the total annual sale including by-product credits would be about 2.01 million dollars.

The calculations of the annualized cash flow were summarized in Table 21. The capital cost and the start-up cost (one month of operating costs) were reflected in the initial year. The plant would operate at 80% of the designed capacity during the first year following construction and in full capacity thereafter. The total project life was 15 years after construction. At the end of that time, 12.5% of the original capital investment, $54,100, would be recovered as salvage. The remaining capital was depreciated over a ten years period of time. In addition, the annual total expenses of the plant were set at $922,630, which included $831,850 of operation cost and $90,780 for sale and overhead as given in Table 19. Also, a 35% total tax rate, including both the federal and provincial taxes, was used in the calculation.

The first column in Table 21 lists the year number, the other headings represents:

- ATC – Annual Total Capital Investment.
- AS – Annual Sale.
- ATE – Annual Total Expenses (operation cost).
- AD – Annual Depreciation, at a rate of (10-*t*)/55 for the year *t* over ten years.

- AT – Annual Tax = 0.35*(AS–ATE–AD).
- ANCF – Annual Net Cash Flow = AS–ATE–AT.
- +ANCF – Accumulated Annual Net Cash Flow.
- r – Return (discount) rate to investors.
- fd – depreciation factor = $1/[(1+r)^t]$, for the year t.
- ADCF – Annual Discounted Cash Flow = fd*ANCF = $ANCF/[(1+r)^t]$.
- +ADCF – Accumulated Annual Discounted Cash Flow.

Three different scenarios of investment return rate or discount rate are presented in Table 21, and also plotted in Figure 11. They are 0% (net cash flow), 10% discount rate, and the maximum return rate. Based on the projected annual sales and costs, the plant would show an after tax profit (net cash flow, ANCF) of over $700,000 each year when in full operation. Over the plant book life of 15 years, the total (accumulated) net cash flow (+ANCF) would be over $10 millions. In the last three columns of Table 21, the maximum return rate was calculated by minimizing the Accumulated Discounted Cash Flow (i.e., setting +ANCF = 0 over the plant life). The maximum return rate of investment was found to be nearly 149%. The high value of the maximum return rate indicates that the CME project will potentially be a profitable operation for investors.

Table 21. Annualized Cash Flow and Maximum Return Rate of Investment (in $Can 1,000).

Year	ATC	AS	ATE	AD	AT	r=0%		r=10%			r(max)=149%		
						ANCF	+ANCF	fd	ADCF	+ADCF	fd	ADCF	+ADCF
1	433	0	0	0	0	-433	-433	0.91	-394	-394	0.40	-174	-174
2	0	1608	738	69	280	590	157	0.83	487	94	0.16	95	-79
3	0	2010	923	62	359	728	885	0.75	547	641	0.06	47	-32
4	0	2010	923	55	361	726	1611	0.68	496	1137	0.03	19	-13
5	0	2010	923	48	364	724	2335	0.62	449	1586	0.01	8	-5
6	0	2010	923	41	366	721	3056	0.56	407	1993	0.00	3	-2
7	0	2010	923	34	369	719	3774	0.51	369	2362	0.00	1	-1
8	0	2010	923	28	371	716	4491	0.47	334	2696	0.00	0.5	-0.3
9	0	2010	923	21	373	714	5205	0.42	303	2999	0.00	0.2	-0.1
10	0	2010	923	14	376	712	5917	0.39	274	3274	0.00	0.1	-0.1
11	0	2010	923	7	378	709	6626	0.35	249	3522	0.00	0	0
12	0	2010	923	0	381	707	7333	0.32	225	3747	0.00	0	0
13	0	2010	923	0	381	707	8040	0.29	205	3952	0.00	0	0
14	0	2010	923	0	381	707	8747	0.26	186	4138	0.00	0	0
15	0	2010	923	0	381	707	9453	0.24	169	4307	0.00	0	0
16	-54	2010	923	0	381	761	10214	0.22	166	4473	0.00	0	0

ATC: Annual Total Capital Investment; AS: Annual Sale; ATE: Annual Total Expenses; AD – Annual Depreciation; AT: Annual Tax; ANCF: Annual Net Cash Flow; +ANCF: Accumulated Annual Net Cash Flow; r – Return (discount) rate; fd: depreciation factor; ADCF – Annual Discounted Cash Flow; +ADCF: Accumulated Annual Discounted Cash Flow.

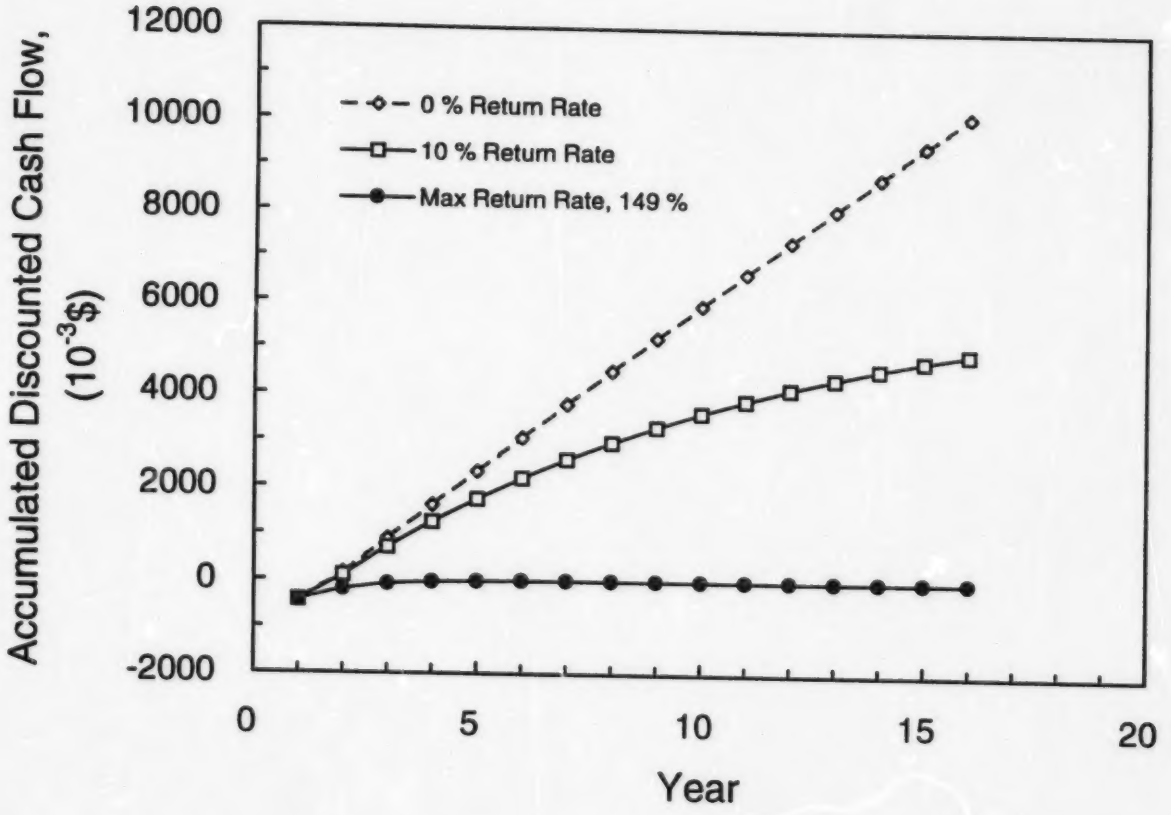

Figure 11. Investment Return at Different Return Rates.

5. Summary and Conclusions

Task 1. Biodiesel Ester Preparation

Methodologies have been developed for the batch scale conversion of vegetable oils to their lower alkyl esters through transesterification. As a result, from four different oils and four lower alkanols, a total of 12 different biodiesel esters have been prepared. They are canola methyl, ethyl, 2-propyl and butyl ester (CME, CEE, CPE and CBE), rapeseed methyl and ethyl ester (RME and REE), linseed methyl, ethyl, 2-propyl and butyl ester (LME, LEE, LPE and LBE), and sunflower methyl and ethyl ester (SME and SEE).

Methyl esters can be prepared fairly easily with high yield. The reaction occurred quickly at ambient temperature with either potassium hydroxide (KOH) or sodium methoxide (CH_3ONa) as the catalysts. Using an oil to anhydrous methanol molar ratio of 1:3 and a catalyst concentration of 0.5 wt% for KOH (or 0.25 wt% for CH_3ONa) in each step, following a two-step process with the removal of glycerol intermittently, over 97% yield to methyl ester was achieved.

The transesterification to ethyl, 2-propyl and butyl esters required progressively severer and costlier conditions. Ethyl esters were made using 0.5 wt% sodium methoxide catalyst between 60 to 70°C, with an oil to anhydrous ethanol molar ratio of 1:6 in a single step reaction. The reaction temperatures were further increased to 72°C for 2-propyl and 105°C for butyl esters, respectively. Metal sodium was utilized as the catalyst by dissolving in respective anhydrous alcohol to form alkoxide anions acting as the catalytic species.

Task 2. Biodiesel Ester Characterization

The chemical, physical and fuel properties of the biodiesel esters have been extensively characterized. The esters were generally very pure, containing none or trace amount (in the cases of CPE and LPE) of mono- and diglyceride impurities. Such a high purity warranted the accuracy of the lubricity data from the M-ROCOL tests. The densities of various esters at 25°C were approximately constant at 0.86 to 0.89 g/ml. Their dynamic viscosities at 40°C were varied from 3.32 to 7.60 cP, which were substantially reduced in comparison to those of the vegetable oils (22 to 45 cP). The average iodine values, indicating the degree of unsaturation, were 108, 113, 142, and 211 for rapeseed, canola, sunflower and linseed esters, respectively. The highest iodine value of the linseed esters was due to the presence of linolenic acid, a triple double bonded fatty acid, as its major constituent. The acid numbers of the esters varied from low 0.15-0.16 mg KOH/g for REE and CME to the highest of 0.61 mg KOH/g for SEE. The cloud points of the methyl and ethyl esters were 1 to –2°C, while those of the butyl esters were reduced to –10 (LBE) and –6°C (CBE), respectively. CBE had the lowest pour point of –16°C among the 12 esters, while SEE indicated the highest pour point of –5°C. The two rapeseed esters, RME and REE, also showed much lower pour point of –15°C. The gross heat of combustion of the esters, measured by bomb calorimetry, ranged from 39.56 MJ/kg (CPE) to 40.97 MJ/kg (REE). These values were the same or slightly higher than those of the pure vegetable oil.

Biodiesel esters had many comparable properties with the conventional diesel fuels. For instance, the esters had less than 10% differences in density as the diesel fuels,

and the differences in viscosity were often no more than 2 folds. The cold flow properties of the biodiesel esters, especially the butyl esters, were comparable to those of the summer diesel fuel; although the winter diesel fuel, being very light, had much lower cloud and pour points than those of the esters prepared. In addition, the heat energy in a full tank of biodiesel was only 9 to 4% lower than that in the conventional diesels. The biodiesel was much less volatile than the diesels, and this feature could make them safer in storage and transportation.

Task 3. M-ROCLE Lubricity Evaluation

All 12 biodiesel esters were combined at 1 vol% treat rates with a reference fuel for the evaluation of the wear scar area (WA), coefficient of friction (CF) and Lubricity Number (LN) of the blended fuels. All biodiesel additized fuels resulted in wear scar areas smaller than that of the reference fuel, with the smallest for CME (WA of 0.200 mm^2). Except for LBE, all the biodiesel additized fuels were also found to reduce the friction, and the two 2-propyl esters (CPE and LPE) had the lowest friction of all the biodiesel additives prepared. The LN is based on the ratio of wear area stress to coefficient of friction, and a diesel fuel of acceptable lubricity should obtain a LN of 1.0 or higher. All 12 biodiesel esters at the 1 vol% treat rate increased the LN of the reference fuel to above the passing level of LN = 1.0. The most effective additive was CPE with a LN = 1.36, mainly because of a very small friction coefficient. CME was the second best performer with a LN = 1.29. It produced the smallest wear scar areas in the M-ROCLE test. The boost in lubricity for the CPE and CME at the 1 vol% treatment rate were 67% and 58%, respectively.

Both CME and CPE were also evaluated at lower treat rates and continued to be effective. For instance, blending 0.1 vol% CME to the reference fuel resulted in a fuel LN of 1.05, again it surpassed the threshold LN of 1.0. A linear semi-log relationship has also been established between the LN and the treat rate of CME and CPE from 0.1 vol% up to 100 vol% (neat esters).

Task 4. Process Development and Economic Analyses.

Based on its lubricity enhancement and production cost, we have chosen canola methyl ester as the best candidate for a lubricity additive.

Accordingly, a continuous flow process for producing canola methyl ester was developed. The process utilized canola seed and methanol as the feed stocks to produce methyl ester, and recovered glycerol and canola meal as by-products. In the design, excessive methanol required for the reaction was recycled and process water was minimized, so the plant would be "cleaner" to the environment.

The costs associated with the production as well as the potential investment returns were also assessed. For an annual production of 1 million liters of canola methyl ester plant, the total capital investment was projected at 350,000 Canadian dollars; the production cost was estimated at $0.72 per liter of ester. Among many factors, the raw oilseed price was found to have the greatest impact on the production cost. To create and occupy new lubricity additive market, selling CME through bulk distribution is more effective than retail distribution. Based on a profit of one dollar per liter of CME on wholesale level, the calculated maximum return rate of investment was 149%. The high value promised a profitable investment on the CME project.

6. Further Development

Significant progress in the laboratory bench scale production and testing of the canola methyl ester has been made. Still, more work is needed in order to achieve the goal of developing the ester into a premium fuel lubricity additive. As to the next phase of research and development, the focus will be on the pilot-scale demonstration, product/process development and consumer introduction of the new product.

We have submitted our phase II research proposal to the ADF. The objective of the proposed project is to cost effectively scale up the production of canola methyl ester and to test its use as diesel fuel lubricity additive in diesel engines. This objective will be achieved systematically by using the following methodology:

- Produce CME in small quantity (1-2 L) and monitor impurities such as glycerol and alkali residual in the ester.
- Determine the "no-harm" influence of different impurities on the performance of direct injected (DI) diesel engines.
- Optimize the process conditions, based on purity and cost tolerance, for industrial ester production.
- Scale up the production of CME to 10 L per day in a pilot plant using the continuous flow process model developed in the present project.

We believe that at the end of this phase II project, we will have the production capacity and technical know-how to make large quantities of canola methyl ester. Data collected from pilot plant runs will be used to improve the plant designs and to estimate more precisely the economics of the process. These will enable us to better convince industry partners and potential investors for commercial development of this product.

7. Benefits to Producers, Processors and Government

Development and creation of a canola oil based fuel additive industry in the Province will bring economical, social and environmental benefits to producers, processors and government in a number of ways.

Production of a canola based additive will expand markets for canola crops. The canola acreage is dropping in recent years because of a number of factors, including transportation bottlenecks. A further one million acres reduction in Western Canada is expected in year 2001 (49). Use of canola oil for fuel additive production would ease this trend. Each year, about 40 billion liters of diesel fuel are used just in Canada. If all the diesel fuel in Canada includes 0.1% canola based additive, this would generate a new market for 250,000 acres of canola (50).

A local operation of canola ester plant will improve the canola oil price for local producers. The major market for edible canola oils are in oversees. Often, because of the transportation bottleneck, the cash price of canola is unable to catch up to the future's price, causing loss to the growers (49). If canola methyl ester plant is operated in the Prairie using locally available raw materials, producers would have no delivery problems. They could sell oilseeds at better prices, in additional to savings on transportation costs.

When a canola based additive production unit is affiliated with existing oilseed crushing plants, equipment that are currently not operating at full capacity would be utilized. A value added new product will create new jobs and bring new revenues to oilseeds processors as well as to the producers.

The advent of industrial oil production in Saskatchewan could also be combined with a process to utilize waste oils and fats from restaurant and food industries. In this

case, the used edible oils would be converted to fuel additives, high temperature grease and other value added products. This would effectively deal with the land and water pollution problems associated with lipid waste disposal.

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D. PERSONNEL

Dr. Ajay K. Dalai (Principal Investigator), Drs. Narendra N. Bakhshi, Martin J. Reaney and P. Barry Hertz (Supervisors), Dr. X. Lang (Postdoctoral Research Associate), and Mr. J. Munson (Graduate Student) have been dedicated for this important project.

E. EQUIPMENT

A BUCHI Rotovapor, model R-114, was purchased for $4,500 for the project, with the prior written approval from ADF.

F. PROJECT DEVELOPMENT MATERIAL

None.

G. PROJECT PHOTOS

None.

H. ACKNOWLEDGEMENT

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I. EXPENSE STATEMENT

Statement of expenses will be forwarded from the University Business Office.